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DETERMINATION OF NITROGEN IN THE ANALYSIS OF AGRICULTURAL PRODUCTS.*

BY S. W. JOHNSON AND E. H. JENKINS.

In 1872, one of us found† that the mixture of caustic soda and caustic lime known as "soda-lime," and used in chemical analysis to determine nitrogen quantitatively, might be replaced by a much more easily prepared mixture of equal volumes of dry sodium carbonate and slaked lime. There is some difficulty in obtaining sodium carbonate suitable for this use. The super-carbonate, which can be readily dried, often contains nitrogen, and the crystals of sal-soda that, after washing, are free from nitrogen, cannot be quickly dried to a *fine* powder. After various trials, the following process of preparing an effective soda-lime was devised:

Equal weights of sal-soda, in clean (washed) large crystals, and of good white and promptly-slaking quick-lime, are separately so far pulverized as to pass holes of $\frac{1}{16}$ inch, then well mixed together, placed in an iron pot, which should not be more than half filled, and gently heated, at first without

* From the Report of the Connecticut Agricultural Experiment Station for 1878 Communicated by the Authors.

† Amer. Chemist, vol. iii, p. 161.

stirring. The lime soon begins to combine with the crystal water of the sodium carbonate, the whole mass heats strongly, swells up, and in a short time yields a fine powder, which may then be stirred to effect intimate mixture and to dry off the excess of water, so far that the mass is not perceptibly moist and yet short of the point at which it rises in dust on handling. When cold it is secured in well-closed bottles or fruit-jars, and is ready for use.

During the past year a large number of comparative analyses have been made on bone-dust, dried blood, fish-scraps, guano, maize-meal, zein or maize-fibrin, and egg-albumin, using soda-lime obtained as above described, and soda-lime either prepared by ourselves according to the directions of Varrentrap and Will, obtained by purchase (Merck's) or kindly supplied by W. M. Habirshaw, Esq., Chemist to the New York State Agricultural Society. These analyses have proved that the new soda-lime gives perfectly satisfactory results in all cases when soda-lime can be employed, or, at least, results perfectly agreeing with those obtained by the help of the soda-lime as usually prepared. It is not needful to adduce analyses here in support of this statement, since its truth will appear from the soda-lime combustions to be shortly given, all of which were made with this new mixture.

This soda-lime is to be recommended for the reasons that the materials for making it, sodium monocarbonate and quicklime, are everywhere procurable in a state of purity, the preparation of many pounds of the mixture may be accomplished in an hour or two with little trouble, and the resulting soda-lime is extremely convenient to use, not absorbing moisture in the mixing, and never swelling in the tube to obstruct it on application of heat.

The controversy that has been so actively prosecuted of late years as to the applicability of the soda-lime method of determining nitrogen to the analysis of albuminoid matters, has led us to review the entire subject as far as possible. It is well known to chemists that a number of experimenters, viz. Nowack, Seegen, Nencke, Liebermann, Voelcker, and Musso, have failed to obtain with the soda-lime method as high results on flesh, milk, and similar substances, as by the use of the so-called absolute method, in which the organic body is

burned with copper oxide and its nitrogen directly measured in the state of gas. Even Ritthausen, who has stoutly maintained the correctness of the soda-lime method, having employed it in his elaborate researches on the vegetable albuminoids, has very recently admitted that it fails to give all the nitrogen of some of this class of bodies, and has fallen back on the absolute method as the only one to be depended upon.

Since it is a matter of high importance in agricultural and physiological work to use the most exact and especially the most trustworthy methods, we have endeavored to investigate the correctness of both modes of analysis, to study the sources of error to which they are severally subject, and to learn what is essential to bring out the greatest accuracy they are susceptible of.

We have been led to the conclusion that with the substances above named, both methods when properly worked give nearly accordant results. Dried blood, dried white of egg and maize-fibrin (crude, obtained by Ritthausen's methods) containing 12 or more per cent. of nitrogen, have yielded us from one to two-tenths of a per cent. less of nitrogen by the soda-lime combustion than by the absolute method. Our observations satisfy us, moreover, that this discrepancy is no more due to any fault of the soda-lime process than to the errors of the absolute method; errors caused, probably, by the impossibility of removing the last traces of common air from the mixture, either by long-continued transmission of pure carbonic gas or by exhaustion with the Sprengel mercury pump, or by both conjointly.

The following results of analyses by both methods are offered to sustain our assertions. We have not selected these analyses to establish the point, but give all the results we have obtained since learning the best mode of conducting the analytical processes, and they fairly represent what the two methods can accomplish when applied with suitable precautions:

	By the Absolute Method.	By Soda lime.	Average difference.
Egg Albumin,	12.54 per cent.	12.34 per cent.	.17 per cent.
	12.51 "	12 36 "	
	12.56 "	12 38 "	
	12 44 "		
	12.59 "		

	By the Absolute Method.	By Soda-lime.	Average difference.
Maize Fibrin (crude)	13.73 per cent.	13 60 per cent.	.13 per cent.
Dried Blood,	11.90 "	11.78 "	
	11.91 "	11.72 "	.12 "
		11.88 "	
" "	7.54 "	7.58 "	.04 "
Fish Scrap,	9.21 "	9.12 "	
		9.02 "	.14 "
		8.64 "	
" "	8.79 "	8.71 "	.11 "
		8.71 "	
Peruvian Guano,	8.27 "	8.21 "	.06 "
" "	8.63 "	8.49 "	
	8.66 "	8.51 "	.15 "
" "	8.21 "	8.13 "	
		8 04 "	.12 "
" "	9.68 "	9.63 "	
		9.67 "	.03 "
" "	7.56 "	7.56 "	
		7.56 "	.00 "

The above analyses illustrate a fact which is general in our experience, viz. that the agreement of several determinations made upon one substance is usually closer by the soda-lime than by the absolute method. This fact goes far to show that the soda-lime process is, to say the least, equal in accuracy with the absolute determination.

The full details of the mode we follow in making an analysis by the absolute method cannot be given here. An outline of the process is as follows :

The substance, mixed with *freshly ignited* copper oxide, is burned in a long glass tube which has been exhausted by means of a mercury pump ; the products of combustion after passing over ignited metallic copper, and *finally over ignited copper oxide*,* are collected in a graduated receiver, containing fifty per cent. solution of caustic potash, and surrounded by a water-jacket. Complete combustion is ensured by heating, in due course, several grams of potassium chlorate at the rear of the tube, three inches of which is bent downward from the horizontal to retain the fused salt. The residual gas is trans-

* The use of a short layer of oxide of copper at the anterior end of the tube was adopted by the writer in 1873, when making analyses of Connecticut tobacco, he having found it impossible to make a blank combustion when using carbonic acid to sweep the tubes, without obtaining unabsorbed gas in the receiver, which proved to be combustible. By burning this gas in the analysis, he was able to get results on uric acid and potassium ferrocyanide agreeing closely with theory and with those obtained by the soda-lime method. More recently, Frankland has adopted this use of copper oxide in nitrogen estimations for water analysis. S. W. J.

Since the above note was printed I have learned that Finkener, in his edition of Rose's Handbuch, anticipated me in this use of copper oxide. S. W. J.

ferred to the receiver by the pump, brought to a constant temperature by a stream of hydrant water and measured in the usual manner. The mercury pump employed is a very effective one, of simple and easy construction, devised for use in this kind of analysis.

With regard to the handling of the soda-lime method the following results have been arrived at:

1. Contrary to what is commonly stated, fine pulverization of the substance to be analyzed is not necessary. If the substance will pass holes of one millimeter in diameter it is fine enough.

A sample of dried blood which passed through a sieve with meshes one millimeter in diameter gave 7.58 per cent. of nitrogen. A portion of the same, ground extremely fine with sand, gave 7.64 per cent.

Fish-scrap passed through the same sieve gave 8.98 per cent. of nitrogen; when ground with sand, 8.95 per cent. A second sample of fish sifted as above gave 8.69 per cent. nitrogen. By the absolute method it yielded 8.79 per cent.

2. Neither the highest heat possible to obtain in an Erlenmeyer gas combustion furnace, nor a long layer of strongly heated soda-lime, nor these two conditions united, occasion any appreciable dissociation of the ammonia formed in combustion.

A sample of dried blood gave 11.42 per cent. of nitrogen when the combustion was made in a tube 14 inches long at a dull red heat.

The same sample yielded 11.56 per cent. when determined in a tube 30 inches long, the mixture occupying 12 inches, and the rinsings and clear soda-lime 16 inches, using as high a heat as possible.

The same experiment was tried with egg-albumin. In a tube 14 inches long it yielded 12.25 per cent.; in one 30 inches long, filled as above, 12.34 per cent.

A superphosphate containing animal matter yielded 3.02 per cent. of nitrogen when the heat was kept quite low, 3.04 per cent. when the heat during combustion was very bright red.

3. The use of pure sugar or of oxalic acid as a diluent does not in any way affect the result.

Dried Blood, 0.5 grams,	gave	10.33	per cent. nitrogen.
" "	with 0.5 grams sugar gave	10.29	" "
" "	" 1.0 " "	10 08*	" "
Dried Blood, "	gave	11.56	" "
" 0.37 grams	with 1 gram sugar gave	11.53	" "
Egg Albumin, 0.5 "	gave	12.51	" "
" 0.4 "	with 0.5 grams sugar gave	12.41	" "
" 0.46 "	" " "	12.50	" "
" 0.3 "	" " "	12.54	" "

Experiments with oxalic acid gave similar results.

4. Iron tubes *of proper length* may be substituted for glass. The results are as satisfactory, but more time is required to make the combustion.

The iron tubes used in the following trials were 22 inches long. They were closed at the rear, and at the end of the combustion were cleared of ammonia by heating a mixture of oxalic acid or sugar and soda-lime, which was kept cool in the rear of the tube till needed for this purpose.

	In glass.	In iron.	
Egg Albumin	12.36	12.25	per cent nitrogen.
Dried Blood	11.42	11.56	" "
Fish Scrap	9.01	8.99	" "
"	8.71	8.68	" "
"	8.66	8.72	" "
Ammoniated Superphosphate	2.69	2.61	" "
" "	2.71	2.68	" "

In the Station Report for 1877 it was stated that combustions in iron tubes yielded 0.2 to 0.5 per cent. less than those in glass. This deficiency was occasioned simply by using too short an anterior layer of soda-lime, the tubes being but 14 inches long. Since iron is a good heat-conductor, these tubes had an effective length much less than glass tubes of the same dimensions would have.

5. A suitable length of the anterior layer of soda-lime must be secured in order to get a good result. With 0.5 gram of substances, such as are encountered in agricultural chemistry, containing less than 8 per cent. of nitrogen, a glass tube of 12 to 14 inches is long enough. As the content of nitrogen increases to 10 per cent. or over, we make the tubes several inches longer. In the combustion of dried blood or egg-albumin we *prefer* a tube 25 to 30 inches long, and the mixture of soda-lime and substance should occupy rather less than half

* In this analysis the combustion was not complete, owing to the large amount of sugar being mixed with insufficient soda-lime.

the tube, a layer of pure soda-lime of 12 or more inches long being essential for perfectly destroying the volatile organic matters.

6. The long anterior layer of pure soda-lime must be brought to a *full red heat* before heating the mixture, and must be so kept throughout the combustion.

7. No fumes or tarry matters, indicative of incomplete combustion, should appear in bulb-tube or receiver.

8. When the combustion proper is begun under the conditions above described, it can be carried on quite rapidly until completed. The contents of the tubes then show no sign of unburned carbon.

9. We get equally good results whether the mixture is made intimately in a mortar, or more roughly by stirring with a spatula in a capsule or scoop, or by mixing in the tube with a wire.

10. We usually allow the glass tube to cool somewhat before aspirating with air to sweep out the ammonia, but have not as yet decided whether this precaution is essential.

11. We receive the ammonia of the combustion in a bulb-tube or flask containing standarded hydrochloric acid, and we measure the excess of acid by a standard ammonia solution, using tincture of cochineal as the indicator.

In conclusion, we recall the fact that some careful experimenters, Ritthausen, Mærcker, Petersen, Kreusler, have repeatedly obtained results nearly as accordant as ours in the use of the two methods. Such results could scarcely be accidental, and we express our conviction that the discrepancies observed by others have been due to imperfect working of the processes. We have had great experience with both modes of determining nitrogen (one of us for twenty-five years), and not until recently have we learned how to be fairly certain of our results on *all* the classes of substances we have had occasion to analyze, either with the soda-lime process or by the absolute method. The purity and uniformly satisfactory qualities of the new soda-lime have greatly facilitated our work. The use of cochineal as an indicator we consider very favorable to exact titration.

ON A METHOD FOR THE DETERMINATION OF PHOSPHORIC ACID.*

By S. W. Johnson and E. H. Jenkins.

Otto long ago proposed a method for the separation of phosphoric acid from iron and aluminum which was based on the fact that ammonium tartrate will prevent the precipitation of the hydrates and phosphates of these metals in alkaline solutions, but does not prevent the precipitation of ammonio-magnesium phosphate.

W. Mayer† has shown that unless a large amount of ammonium salts is present in solution, basic magnesium tartrate will also be precipitated with the phosphate. He prepared a solution for use in the determination of phosphoric acid in which the amounts of magnesium and ammonium salts were in such relation that a precipitation of basic magnesium tartrate was not to be feared. Such a solution cannot be used, however, for the direct gravimetric determination of phosphoric acid in the presence of much lime, because neutral calcium tartrate is apt to be precipitated with the ammonio-magnesium phosphate.

F. Stolba‡ has shown that pure ammonio-magnesium phosphate can be determined by titration as well as by weighing, one molecule of the pure salt requiring two molecules of hydrochloric acid to destroy its alkaline reaction. Advantage has been taken of these observations in devising a plan of operating which should meet the want felt for a rapid and accurate method of determining phosphoric acid in commercial fertilizers. The standard acid used in other volumetric work answers perfectly for this. A strong, nearly saturated, solution of ammonium tartrate, free from carbonic acid, and a solution of some magnesium salt, are also necessary. The latter is prepared by dissolving 70 grams of

* From the Report of the Connecticut Agricultural Experiment Station for 1878. Communicated by the Authors.

† Ann. Chem. Pharm. 101, 164.

‡ Zeitschr. Chemie, xvi, 100.

magnesium sulphate and 195 grams ammonium chloride in 1 liter of water. 10 cubic centimeters of this solution contain twice the amount of magnesium necessary to precipitate 0.1 gram phosphoric acid (P_2O_5). A suitable amount of the phosphate (in most cases 1 gram is a convenient quantity) is dissolved in hydrochloric acid, the solution nearly neutralized with ammonia, and ammonium tartrate solution is added, 10 cubic centimeters at a time, till the solution remains perfectly clear when slightly alkaline. Add a suitable quantity of the magnesium mixture, and either stir vigorously with a rod, or, if the precipitation is made in an assay-flask, as it can be very conveniently, shake occasionally. When the precipitation is nearly complete add enough ammonia to make it very strongly alkaline, and let it stand 6–12 hours. It can then be filtered, preferably on the pump, and washed with equal parts of strong alcohol, 85–90 per cent., and water. No pains are taken to detach the precipitate from the glass. When the dish and precipitate are washed until the washings no longer react alkaline, the filter and precipitate are brought back into the beaker or flask, a *little* water and a few drops of cochineal tincture are added, and it is titrated. This is best done by adding an excess of standard acid at once, stirring so that all the precipitate shall be wetted with it, and after it has stood a few minutes, measuring back with standard alkali.

The results given below (mostly duplicated) indicate the degree of accuracy to be expected.

	Determined by use of ammonium molybdate.	Determined by the method just described.
Superphosphates, soluble phosphoric acid,	8.92–8.96	8.83–8.91
" " "	8.31	8.32
" " "	11.89–11.95	11.83–11.95
" " "	5.14–5.08	5.07–5.11
" " "	6.78	6.68–6.84
" " "	5.63–5.65	5.61–5.63
" total "	9.21–9.28	9.22–9.32
" " "	10.70–10.72	10.76–10.87
* " " "	16.66–16.66	16.55–16.65
* " " "	13.94	13.90–14.05
Hair Manure, . . " "	2.23	2.19 ....
Bone, ... " "	21.90–21.90	21.87–21.75
" . . . . " "	13.21–13.40	13.19–13.33
" . . . . " "	22.57–22.62	22.57–22.76
" . . . . " "	21.90–21.90	21.87–21.75
Fish Scrap, . . " "	6.17–6.27	6.17–6.28

* Navassa superphosphates containing soluble iron and aluminum phosphates.

	Calculated.	
Tricalcic phosphate with 6.44 per cent. water,	42.85	42.79
The above (0.5 gram) with 0.22 gram iron in form of ferric chloride	42.85	42.79

In the case of a few phosphatic materials rich in phosphoric acid, larger discrepancies than any above given have been occasionally encountered, and it is proposed to give them further attention, although it is our impression that they were accidental and do not invalidate the accuracy of the method.

This process requires less than half the time and labor necessary for the molybdic method, is scarcely less accurate and appears to be generally applicable.

Some investigations, not completed as yet, lead us to hope that ammonium tartrate may be successfully substituted for ammonium citrate for bringing precipitated or reverted phosphates into solution. This step would still further simplify the analyses of superphosphates, since the entire phosphoric acid, soluble, reverted and insoluble, could be quickly estimated in a single portion.

Our investigations have also demonstrated that while ammonio-magnesium phosphate is totally insoluble in a large excess of ammonium tartrate, it is soluble in excess of ammonium citrate, and hence all methods based on the use of citric acid are faulty.

It is a fact also that ammonio-magnesium phosphate is largely soluble in ferric and aluminic solutions, containing *insufficient* ammonium tartrate.

It is therefore necessary in presence of iron to add ammonium tartrate more than enough to produce a reddish-yellow solution, enough in fact to make a greenish-yellow solution, as Otto has indicated. A similar excess of ammonium tartrate is also requisite in presence of aluminum, and while there is no color-indication of the suitable quantity, a large excess does not appear to retain ammonio-magnesium phosphate in solution, unless the liquids are too concentrated.

EXAMINATION OF THE NORTH CAROLINA URANIUM MINERALS.

By F. A. Genth.

Prof. W. C. Kerr describes the occurrence of uranium minerals in Mitchell County, North Carolina, as follows:* "A new locality, the Flat Rock mine, recently visited, has yielded the following in immediate association, viz. uraninite, gummite, uraconite, and, as incrustations on the outside of the latter, and of the fragments of rock adjacent, torbernite and autunite. These minerals occur only in one part of the mica-bearing portion of a very large granite vein, and are found in irregular nodules and rounded masses, some with a nucleus of uraninite of ¼ to ¾ inch, enveloped with a heavy layer of gummite, outside of which is a pale, yellow, earthy coating from ¼ to ½ of an inch thick, which is uranochre or uraconite. One lump, the largest, weighs just a pound, and in all, I obtained between 3 and 4 pounds. The quantity of pitchblende, remaining unaltered is very small, and by far the greater part of the mass of the nodules, probably nine-tenths, is gummite; and the smaller ones are nearly or entirely changed to uraconite."

Through the kindness of Prof. Kerr I have recently come into possession of specimens of this highly interesting occurrence, which fully agree with the description above quoted. As his mineralogical determinations, however, were not supported by chemical analysis, and, especially as the composition of gummite is very doubtful, I thought that an investigation of the uranium minerals from this locality would be desirable.

I regret that of the uraninite no material for analysis could be obtained. One of my specimens of gummite, however, still contains one or two small fragments of uraninite; the larger one has a brownish black color, on the margin changing into brownish and, by degrees, into the pure gummite. It is also penetrated by small veins, showing the gradual alteration of the uraninite.

* Am. Journ. Sc. [3] xiv, 496.

Uranotil.—E. Boricky.

The analysis of the pale yellow coating surrounding the gummite shows that it is a variety of *uranotil*, and *not uranochre* or *uranoconite*. The original uranotil has been found in cavities of quartz, associated with fluorite at Wœlsendorf in Bavaria, in lemon-yellow, rhombic needles of a specific gravity of 3.95. For comparison I will give below Boricky's analysis of it.

The North Carolina variety is apparently amorphous; massive, compact. H = 2.5. Sp. gr. = 3.834. Lustre waxy to dull; color from pale straw-yellow to lemon-yellow; streak pale straw-yellow; opaque; fracture uneven.

B. B. in a tube yields water and becomes brownish yellow; with fluxes the uranium reactions. Easily soluble in chlorhydric acid; on evaporation yields a jelly of silicic acid.

The analyses gave, after deducting a small quantity of quartz, mica and feldspar:

			Mean.	Boricky.	Calculated.
SiO_2	= 13.55 ...	13.88 ...	13.72 ...	13.78 ...	13.95
Al_2O_3 & Fe_2O_3	= traces ...	traces ...	traces ...	0.51 ...	.....
UO_3	= 66.76 ...	66.59 ...	66.67 ...	66.75 ...	66.98
PbO	= 0.74 ...	0.45 ...	0.60 ...	... ...	...
BaO	= 0.28		0.28 ...	... ...	...
SrO	= 0.13	... 0.48	0.13 ...	... ...	...
CaO	= 6.23 ..	7.11 ...	6.67 ...	5.27 ...	6.51
P_2O_5	= not det'd	0.29 ...	0.29 ...	0.45 ...	...
H_2O	= not det'd	12.02 ...	12.02 ...	12.67 ...	12.56
		100.82	100.38	99.43	100.00

Rammelsberg* gives for uranotil the formula $Ca_2(UO_2)_6Si_5O_{18} + 15H_2O$. My analyses agree far better with the following formula $Ca_3(UO_2)_6Si_6O_{21} + 18H_2O$, as will be seen from the above calculated analysis. It forms an incrustation upon gummite and results from its alteration, sometimes (as has been observed by Prof. Kerr) changing the entire mass of the latter and yielding nodules of pure uranotil; mostly, however, converting not only the outside of the gummite into uranotil, but penetrating its whole mass, so that even the purest particles contain already a large percentage of it, as will be seen from the analyses of the gummite.

* Mineralchemie, 692.

Gummite.

The orange-colored mineral from the Flat Rock mine has been called gummite, from its resemblance to that from European localities. It occurs in amorphous, compact, nodular masses. H = 3. Sp. gr. = 4.840. Lustre faintly resinous to dull; color reddish yellow to deep orange red; streak orange yellow; opaque; fracture subconchoidal to uneven.

B. B. yields water and turns reddish brown; upon charcoal with sodium carbonate yields metallic lead, with fluxes gives the reactions of uranium. Easily soluble in acetic acid.

Below I give the analyses of the purest, deep orange red material, after deducting a minute quantity of quartz, feldspar and mica. For comparison I add the only analysis which is known of gummite, that from Johann-Georgenstadt in Saxony, by Kersten:

					Mean.	Johann-Georgenstadt. Kersten.
SiO_2	= 4.49 ...	4.83 ...	4.58 ...	4.63	...	4 26
Al_2O_3	= 0.67 ...	0.40		0.53	Mn_2O_3	0.05
BaO	= 0.98	1.12	[4.59]	1.08	As, Fl	traces.
SrO	= 0.05				...	...
CaO	= 1.96 ...	2.14	...	2.05	...	6.00
PbO	= 5.48 ...	5.58 ...	5.64 ...	5.57	...	...
UO_3	=[75.71]...	75.50 ...	74.39 ...	75.20	...	72.00
P_2O_5	= 0.12 ...	0.07 ...	0.16 ...	0.12	...	2.30
H_2O	= not det'd	10.43 ...	10.64 ...	10.54	...	14.75
		100.07		99.72		99.36

The opinion of chemists as to the composition of gummite is very much divided. Kersten thought it to be a combination of phosphate of lime with uranic hydrate, the composition of which he expressed by the formula $3CaO,P_2O_5 + 4U_2O_3,9H_2O$. Berzelius considered it as a mixture of basic phosphate and basic silicate of uranic oxide and lime. Hausmann takes it to be principally the hydrate of uranic oxide. Rammelsberg expresses the same opinion, but believes that the analyses of gummite, together with those of eliasite and pittinite, represent mixtures, and that from their analyses no rational composition can be derived. Hermann, on the other hand, considers these and other uranium minerals, in which silicic acid has been

found, even uraninite, as definite compounds of the formula: $4RO,SiO_2 + 4(4R_2O_3,SiO_2) + mH_2O + nX$. The accessory molecule X being wanting in pittinite, and in the other species represented by R(AsS) in uranochalcite, by $4RO,U_2O_3$ in uraninite, by CaO,CO_2 in eliasite, by $3CaO,P_2O_5$ in phosphor-gummite, and by $3CaO,(PV)_2O_5$ in vanadin-gummite. Hermann's views are as untenable as those of the others. Nearest to the truth, in my opinion, comes Patera, who holds that silicic acid and phosphoric acid are not essential, and that gummite is principally a lime-uranate, $CaO,2U_2O_3 + 6H_2O$, analogous in composition to the artificial uran-yellow.

Gummite is the result of an alteration of uraninite, and it seems to me that both pittinite and eliasite are intermediate between the two, containing more or less of either. But I have already pointed out the fact that the gummite from North Carolina is a mechanical mixture, and that uranotil penetrates the whole mass. The gradual change from gummite into uranotil can be observed on every specimen from this locality.

If we calculate from the SiO_2 in the gummite the requisite constituents of uranotil, making up the minute deficiency of CaO by its equivalent of BaO, we get:

SiO_2	=	4.63
CaO	=	2.05
BaO	=	0.30
H_2O	=	4.17
		33.38 per cent. of uranotil.

The PbO and BaO may be most rationally considered as being present in the form of $\dot{M}(UO_2)_2O_3 + 6H_2O$; we get therefore

PbO	=	5.57
UO_3	=	14.39
H_2O	=	2.70
		22.66 per cent. of lead-uranate; and
BaO	=	0.78
UO_3	=	2.93
H_2O	=	0.55
		4.26 per cent. of barium-uranate.

There remain 35.65 per cent. of UO_3, which is evidently present as uranic hydrate, requiring 4.45 per cent. of water.

The gummite from the Flat Rock mine is therefore a mechanical mixture of:

Uranic hydrate	=	$H_2(UO_2)O_3 + H_2O$	= 40.10 %
Uranotil	=	$Ca_3(UO_2)_6Si_6O_{21} + 18H_2O$	= 33.38
Lead-uranate	=	$Pb(UO_2)_2O_3 + 6H_2O$	= 22.66
Barium-uranate	=	$Ba(UO_2)_2O_3 + 6H_2O$	= 4.26
			100.40

The analyses of pittinite and eliasite admit of no calculation as they appear to have too many foreign substances present, and as the amount of uranous oxide which they evidently contain has not been determined; if we take the analysis of gummite from Johann-Georgenstadt, we find it probably to be a mixture of calcium-uranate, with uranotil, a uranium-phosphate (phosphuranylite) and uranic hydrate. These calculations give the following amounts:

SiO_2	=	4.26
UO_3	=	20.45
CaO	=	1.99
H_2O	=	3.84
		30.54 per cent. of uranotil.
CaO	=	4.01
UO_3	=	41.25
H_2O	=	7.73
		52.99 per cent. of calcium-uranate.
P_2O_5	=	2.30
UO_3	=	4.68
H_2O	=	1.75
		8.73 per cent. of phosphuranylite.
UO_3	=	5.62
H_2O	=	0.70
		6.32 per cent. of uranic hydrate.

The gummite from Johann-Georgenstadt has therefore probably the following composition, corresponding with Kersten's analysis:

Uranic hydrate	=	$H_2(UO_2)O_2 + H_2O$	=	6.32 %
Uranotil	=	$Ca_3(UO_2)_6Si_6O_{21} + 18H_2O$	=	30.54
Phosphuranylite	=	$(UO_2)_3P_2O_8 + 6H_2O$	=	8.73
Calcium-uranate	=	$Ca(UO_2)_2O_3 + 6H_2O$	=	52.99
				98.58

Phosphuranylite.—A new species.

Rhombic (?). Under the microscope very minute rectangular scales with pearly lustre can be distinguished. In pulverulent incrustations upon quartz, feldspar and mica. Color deep lemon-yellow.

B. B. in the tube yields water and becomes reddish brown while hot, brownish yellow after cooling; readily soluble in nitric acid, yielding with ammonium molybdate a yellow precipitate; contains *no* arsenic acid.

As this mineral is very rare, only a very minute quantity could be obtained which was free from autunite; this being in the form of a thin coating upon quartz, both together had to be taken as material for analysis.

0.6705 grams contained 0.5617 grams quartz — the analysis was therefore made with 0.1088 grams of material. This was slightly mixed probably with cerussite, which was visible under the microscope in the form of very small colorless particles. In the first column I give the results of the analysis, in the second the percentage of the phosphate, excluding the lead oxide, and in the third the calculated percentage, corresponding to the formula given below.

						Calculated.
UO_3	=	71.73	...	76.71	...	77.56
PbO	=	4.40	...	...	...	...
P_2O_5	=	11.30	...	12.08	...	12.75
H_2O	=	10.48	...	11.21	...	9.69
		97.91				

It will be seen from this analysis that the uranium and phosphorus are present exactly in the ratio of 3 : 2, and that

the composition of phosphuranylite may be expressed by a formula analogous to that of troegerite, but containing only half the amount of water:

Phosphuranylite = $(UO_2)_3P_2O_8 + 6H_2O$
Troegerite = $(UO_2)_3As_2O_8 + 12H_2O$.

Prof. Kerr mentions torbernite as one of the uranium minerals from the Flat Rock mine, and he sent me some uranite, which had a deep green color and resembled it very closely; but the chemical examination of one of the darkest green crystals showed that it contained only lime, and not a trace of copper oxide, and that the uranite from this locality is therefore only autunite.

UNIVERSITY OF PENNSYLVANIA, W. Philadelphia, *April* 12, 1879.

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.

No. I.

RESEARCHES ON THE SUBSTITUTED BENZYL COMPOUNDS.*

BY C. LORING JACKSON.

INTRODUCTION.

The existence of the benzyl compounds was first established by Cannizaro,† in 1853; for, although Liebig and Wœhler,‡ in their classical research on the benzoyl compounds, obtained benzylalcohol as a secondary product from the action of potassic hydrate on benzaldehyde, they merely spoke of it as an oily liquid, and did not determine its composition or properties. It was also Cannizaro who, in 1855,§ showed that

* Presented to the American Academy of Arts and Sciences. Communicated by the author.

† Ann. der Chemie, 88, p. 129. ‡ Ib., 3, p. 249. § Ib., 96, p. 246.

toluole, when treated with chlorine, yielded a substance identical with the benzylchloride prepared from benzylalcohol by means of hydrochloric acid. The nature of the action of chlorine on toluole was not, however, thoroughly understood until Beilstein and Geitner,* in 1866, found that chlorine converted cold toluole into chlortoluole, but yielded benzylchloride with boiling toluole. In the same paper they predicted that pure chlorbenzylchloride could be prepared by the action of chlorine either on hot chlortoluole or on cold benzylchloride. Both these methods were tried successfully by Neuhof† in the same year, but the chlorbenzylchloride thus obtained was not the first substituted benzyl compound known, as Beilstein‡ had already obtained the chlorbenzylmercaptan, and Naquet§ the chlorbenzylethylether, from the mixture of dichlortoluoles made by acting upon toluole with chlorine. Immediately after the preparation of chlorbenzylchloride by Neuhof, many of its derivatives were studied by Beilstein and Kuhlberg and Neuhof;‖ and the two former extended their investigations to the chlorbenzyl compounds containing more than one atom of chlorine attached to the benzole ring. Since that time, but little attention has been given to this class of compounds; the only researches being those of Bœhler,¶ and later, Vogt and Henninger,** on the sulphoacids, of Berlin,†† who obtained some curious results from the animes, of Sintenis,‡‡ who investigated the ethers, and of Pauly on the sulphide.§§

Besides these chlorbenzyl compounds, only two other classes of substances lying within the range of this paper have been studied, the nitrobenzyl compounds—the first of which, nitrobenzylchloride, was described by Beilstein and Geitner in 1866, in the papers already referred to;‖‖ its derivatives were further studied by Grimaux,¶¶ Beilstein, and Kuhl-

* Beilstein and Geitner, Ann. der Chemie, 139, p. 331.
† Neuhof, Zeitschr. der Chem., 1866, p. 653.
‡ Beilstein, Ann. der Chemie, 116, p. 346.
§ Naquet, ib., Sup. 2, p. 250. Compt. rend., 56, p. 129.
‖ Beilstein, Kuhlberg, Neuhof, Ann. der Chemie, 147, p. 339; ib., 150, p. 286; ib., 146, p. 319.
¶ Bœhler, Ann. der Chemie, 154, p. 56.
** Vogt, Henninger, Ann. Chim. Phys. [4], 27, p. 130; Ann. der Chemie, 165, p. 362.
†† Berlin, Ann. der Chemie, 151, p. 137.
‡‡ Sintenis, ib., 161, p. 329.
§§ Pauly, ib., 167, p. 187.
‖‖ Beilstein and Geitner, Ann. der Chemie, 139, p. 331.
¶¶ Grimaux, Compt. rend., lxv., p. 211; Ann. der Chemie, 145, p. 46.

berg,* Bœhler,† Strakosch,‡ Czumpelik,§ Radziszewski,‖ Henry,¶ and Jackson;** and a few amidobenzyl compounds, the cyanide prepared by Czumpelik,†† and the animes by Strakosch.‡‡

All these substances belonged to the para series, and no isomeric chlor- or nitrobenzyl compounds were known with the exception, perhaps, of the monochlorbenzylsulphosalts described by Vogt and Henninger,§§ and the isomeric nitrobenzylalcohol obtained by Grimaux‖‖ from nitrobenzaldehyde, until 1876, when the meta- and orthobrombenzylbromides were described in a preliminary notice ¶¶ of a portion of the work contained in these papers. In 1877 Wachendorff published a very interesting paper*** upon the nitrobenzylchlorides and bromides, in which he described the metanitrobenzylbromide, and called attention to the striking facts that metanitrobenzylchloride could not be obtained under conditions which gave without difficulty the paranitrobenzylchloride, and he had not as yet succeeded in obtaining the ortho compounds under any of the conditions which furnished their isomeres.

ON CERTAIN SUBSTITUTED BENZYLBROMIDES.

Parabrombenzylbromide ($C_6H_4^{p}Br.CH_2Br.$). — Preparation. First Method. Ten grams of pure parabromtoluole, melting point 28.5°, (either from the factory of Kahlbaum in Berlin, or of Schuchardt in Gœrlitz) were heated in a paraffine-bath to the boiling-point of parabromtoluole in a small flask, through whose cork passed a return-cooler and the stem of a drop-funnel containing 10 grams of bromine, the end of which within the flask was less than a centimeter above the surface of the bromtoluole; the bromine was allowed to flow in at such

* Beilstein, Kuhlberg, Neuhof, Ann. der Chemie, 147, p. 339; ib., 150, p. 286; ib., 146, p. 319.
† Bœhler, Ann. der Chemie, 154, p. 55.
‡ Strakosch, Ber. d. chem. Gesell., 1872, p. 692.
§ Czumpelik, ib., 1870, p. 473.
‖ Radziszewski, ib., 1870, p. 198.
¶ Henry, ib., 1869, p. 637.
** Jackson, ib., 1875, p. 321.
†† Czumpelik, ib., 1870, p. 473.
‡‡ Strakosch, ib., 1872, p. 692.
§§ Vogt, Henninger, Ann. Chim. Phys. [4], 27, p. 139; Ann. der Chemie, 165, p. 362.
‖‖ Grimaux, Compt. rendus, lxv., p. 211; Ann. der Chemie, 145, p. 46.
¶¶ Jackson, Ber. d. chem. Gesell., 1876, p. 931.
*** Wachendorff, Ann. der Chemie, 185, p. 259.

a rate that it was completely decolorized at a short distance from the end of the tube. If these precautions were observed, the liquid solidified almost completely on cooling, and the substance was easily purified by pressing the crystals thus obtained between filter-paper and recrystallizing once or twice from hot alcohol. The average yield from ten grams of parabromtoluole was ten grams of parabrombenzylbromide, that is about sixty-eight per cent. of the theoretical amount; as the method of purification given above is attended with some loss from the formation of an ethylether it is better, if large quantities of the substance are needed, to distil the product of the reaction with the vapor from an aqueous solution of hydrobromic acid, which gives, after pressing on filter-paper, a product pure enough for ordinary preparation work.

The substance was also obtained from the mixture of para- and orthobromtoluole,* prepared by treating cold toluole with bromine. On cooling the product of the action of bromine on the hot mixture with ice and salt, some parabrombenzylbromide separated out, and more was obtained by distilling off a part of the oil with hydrobromic acid and steam, as the orthobrombenzylbromide distils over more easily than the para compound. This method is not to be recommended, however.

Second Method. Benzylbromide was treated in the cold with an equal weight of bromine, to which a little iodine had been added; on freezing the product of the reaction, a quantity of parabrombenzylbromide separated out. This method is decidedly inferior to that with pure parabromtoluole, as it not only gives a smaller yield, but also there is a possibility that orthobrombenzylbromide may be formed.

The composition of the parabrombenzylbromide was established by the following analyses:

0.5934 gr. of substance gave 0.7377 gr. CO_2 and 0.1378 gr. H_2O.

0.5679 gr. of substance gave, after ignition with CaO, 0.8579 gr. AgBr.

	Required for $C_7H_6Br_2$.	Found.
Carbon	33.6	33.90
Hydrogen	2.4	2.57
Bromine	64.0	64.28
	100.0	100.75

*Ann. der Chemie, 147, p. 39.

Properties.—Crystallized from alcohol, it forms thick colorless needles, with a brilliant lustre; from the oily mother-liquor formed in its preparation or from benzole, it separates on slow evaporation in well-formed prisms, apparently of the orthorhombic system, often a centimeter or more long and two to four millimeters thick, which have the consistency of sublimed sal-ammoniac. Its odor is agreeable and aromatic, but its vapor attacks the mucous membrane with very great violence, causing tears, and running at the nose; it was observed, however, by all who were exposed continually to its action that they became much less sensitive to it after a few days. When brought upon the more delicate parts of the skin it causes a sharp, stinging pain, but produces no such effect on the hands; the taste is extremely biting, causing great pain to the tongue for several minutes; it melts at 61½°, can be distilled with steam, sublimes in needles, and burns with a luminous green-bordered flame. It is almost insoluble in water, although it imparts its odor to it; (the flat needles, mentioned in a preliminary paper* as separating from water by spontaneous evaporation, were undoubtedly the more soluble parabrombenzylalcohol); it is but slightly soluble in cold, freely in hot alcohol, very readily in ether, benzole, carbonic disulphide, and glacial acetic acid. On one occasion it was oxidized very rapidly by a mixture of potassic dichromate and dilute sulphuric acid, the action being attended by flashes of light visible even in diffused daylight, the product was an acid melting in the crude state at 239° to 240°, which must therefore be parabrombenzoic acid.

It seems highly probable that this parabrombenzylbromide is the substance obtained, but not purified or studied by Lauth and Grimaux,† in 1866, in the residue from the distillation of bromtoluole; since they described it as crystallizing in needles, and in the highest degree irritating to the eyes.

Metabrombenzylbromide ($C_6H_4^{m}Br.CH_2Br$) was made from metabromtoluole, prepared by Wroblevsky's‡ method (compare also Grete§), as follows: 30 gr. of the mixture of para- and orthoacettoluid, obtained as a secondary product in Wroblev-

* Ber. d. chem. Gesell., 1876, p. 931.
† Lauth and Grimaux, Bull. Soc. chim. [2], v. p. 347.
‡ Wroblevsky, Ann. der Chemie, 168, p. 153.
§ Grete, ib., 177, p. 231.

sky's process for purifying orthotoluidine, previously reduced to a granular condition by crystallization from boiling water, were suspended in cold water, and 45 gr. of bromine dissolved in water added in small portions at a time, shaking until the yellow color disappeared after each addition; the acetyl group was removed from the metabromacettoluid thus obtained by boiling with fuming hydrochloric acid in a flask with a return cooler; the base, set free by an alkali, was dissolved in portions of 10 gr. at a time in absolute alcohol, and the amido group replaced by hydrogen by Griess's reaction; the alcohol was then partly distilled off on the water-bath; the residue distilled with steam, dried, and rectified, the portion passing over from 179° to 185° being collected. To convert this into metabrombenzylbromide, 10 gr. of it were heated to boiling, and treated with 10 gr. of bromine in the way described under parabrombenzylbromide (see page 95); the metabromtoluole took up the bromine somewhat more slowly than the parabromtoluole. The liquid left after the bromiring was finished was distilled in a current of the vapor from hydrobromic acid (boiling point 125°), prepared according to Naumann,* until a considerable portion had passed over: the flask containing the substance was not heated for fear of decomposition. The hydrobromic acid vapor cannot be replaced by steam; as under these conditions some of the brombenzylalcohol might be formed, although I am inclined to think that this reaction would take place much less readily here than it does in the case of the parabrombenzylbromide. The residue left in the flask was transferred to a funnel-tube, closed with a rubber stopper on a glass rod and surrounded with ice. If the distillation had been carried on long enough, nearly the whole of the oil solidified to a dark, pasty mass. The stopper was then removed, and the brown oil sucked out as completely as possible by means of the Bunsen pump. The white scales left on the funnel were boiled with a small quantity of alcohol; the clear solution poured off from the undissolved oil and cooled in a corked flask. As soon as no more oil was deposited the clear liquid was decanted into another flask and cooled with ice, when crystals were formed. The same process was repeated with the mother-liquor and the residue until the whole

* Naumann, Ber. d. chem. Gesell., 1876, p. 1574.

was converted into crystals; another crop of less pure metabrombenzylbromide was obtained by adding snow to the mother-liquor from the final operation. The crystals were purified by similar crystallization from hot alcohol. It was necessary that all these operations should be carried on in corked flasks, as the metabrombenzylbromide, when moistened with alcohol, evaporated when exposed to the air so rapidly that there was a very considerable loss from working with open vessels.

The composition of the metabrombenzylbromide was established by analysis:

0.4333 gr. substance gave, after ignition with CaO, 0.6609 gr. AgBr.

	Required for $C_7H_6Br_2$.	Found.
Carbon	33.6	34.63
Hydrogen	2.4	2.66
Bromine	64.0	63.96
	100.0	101.25

Properties.—Crystallized from alcohol by cooling, it forms white bladed needles or plates arranged in radiated groups; by slow evaporation of its alcoholic solution, it can be obtained in flat prisms with square ends sometimes reaching a length of 3 cm. and a breadth of 2 mm. It has an agreeable odor, aromatic, but different from that of parabrombenzylbromide, while its action on the mucous membrane is even more violent, perhaps because it is more volatile; its taste and action on the more delicate parts of the skin is similar to that of the para compound; it melts at 41°, can be distilled with steam only very slowly, sublimes in oily drops, and burns with a luminous flame having a green border. One of its most striking properties is that when moistened with alcohol or ether it evaporates very rapidly, whereas when dry it is comparatively fixed. It is almost insoluble in water, but imparts its odor to it, is freely soluble in cold, still more so in hot alcohol, and very readily soluble in ether, benzole, carbonic disulphide, and glacial acetic acid. An oxidizing mixture of potassic dichromate and dilute sulphuric acid seems to be without action on it; but the same mixture converts the alcohol derived from it into an acid, which, in a not perfectly pure state, melted at 151°, and must therefore be metabrombenzoic acid.

Orthobrombenzylbromide ($C_6H_4\overset{o}{Br}.CH_2Br$.).—After several unsuccessful attempts to obtain an orthobromtoluole free from the para compound from the mixture prepared by adding bromine to cooled toluole, I decided to insure a perfectly pure substance as my starting-point by making the orthobromtoluole from orthotoluidine. The first method employed for purifying the orthotoluidine was that of Wroblevsky,* by boiling crude toluidine sixteen hours with glacial acetic acid; but all the samples obtained by this process contained traces of paratoluidine. After I had convinced myself by experiment that the methods of Rosenstiehl,† by treating the oxalates with ether; and of Beilstein and Kuhlberg,‡ by precipitating an acetic acid solution of acettoluid with water,—were almost impracticable for large quantities, I tried the method of Schad,§ recommended by Kekulé,‖ which depends on the crystallization of the nitrates and chlorides, and in this way succeeded in obtaining a liquid toluidine which with acetylchloride gave an acettoluid melting after one recrystallization from boiling water at 107°. As some previous attempts to convert orthotoluidine into orthobromtoluole by the usual method through the diazoperbromide had given me as unsatisfactory a yield as that obtained by Wrobvesky,¶ I treated this according to a new modification of the process of Huebner and Majert** for preparing parachlortoluole, which I had found to work admirably in making that substance. This modification was suggested by Victor Meyer's†† method of applying Griess's reaction, and consisted in dissolving 20 gr. of the orthotoluidine in an excess of hydrobromic acid (boiling point 125°, prepared according to Naumann‡‡); the pasty mass was then treated with somewhat more than the calculated amount of solid potassic nitrite, which was added in small portions at a time, the flask being corked after each addition, and shaken until all the red fumes were absorbed; after the last portion of nitrite had been added, the greater

* Wroblevsky, Ann. der Chemie, 168, p. 162.
† Rosenstiehl, Zeitschr. Chem., 1868, p. 557, 666.
‡ Beilstein, Ann. der Chemie, 156, p. 75.
§ Schad, Ber. d. chem. Gesell., 1873, p. 1361.
‖ Kekulé, Ber. d. chem. Gesell., 1874, p. 1006.
¶ Wroblevsky, Ann. der Chemie, 168, p. 171.
** Huebner and Majert, Ber. d. chem. Gesell., 1873, p. 794.
†† V. Meyer, Ber. d. chem. Gesell., 1875, p. 1074, note.
‡‡ Naumann, Ber. d. chem. Gesell., 1876, p. 1574.

part of the liquid was distilled off, and the residue then treated again in the same way. The distillate consisted of dilute hydrobromic acid and a heavy oily liquid which was separated with a drop-funnel, washed with potassic hydrate solution until the odor of cresole was removed, then with water, and finally dried and rectified; in this way 40 grams of orthotoluidine gave 29 grams of crude orthobromtoluole, and 24 grams of this gave on the first fractioning 19 grams of a colorless liquid boiling between 179° and 182°; that is, about thirty-six per cent. of the theoretical yield, whereas the diazoperbromide furnishes under the best conditions only ten per cent. The new method has the further advantages of taking much less than half the time occupied by either of the old ones, and the product is not contaminated with the nitro compounds which compelled Huebner and Majert to reduce before rectifying. Von Richter* has also obtained tetrabrombenzole by the action of nitrous anhydride on a mixture of tribromaniline with hydrobromic and glacial acetic acids; he ascribes the reaction to the presence of the negative atoms, and announces his intention of trying similar experiments with compounds containing fewer bromine atoms or nitro groups; that the reaction is not due to the presence of such negative radicals is proved by the previous researches of Huebner and Majert, which he seems to have overlooked, and the results given above. I should not have intruded on von Richter's field of work had it not been necessary for me to obtain the orthobromtoluol, but I felt the less hesitation in doing so, as I am unable to see that his method differs in any essential particular from that of Huebner and Majert, published nearly two years before the appearance of his article.

The orthobromtoluole was converted into orthobrombenzylbromide by treatment with bromine in the way described under the para compound. The purification of the substance was a matter of some difficulty, as it seemed to be completely decomposed by rectification, and converted into the alcohol by distillation with steam; the method finally adopted was distillation in a stream of the vapor from aqueous hydrobromic acid, as described under the metabrombenzylbromide; the first fifth of the distillate was rejected to make sure of the

* Von Richter, Ber. d. chem. Gesell., 1875, p. 1428.

absence of orthobromtoluole; that which came over later was washed till it ceased to give an acid reaction, and then dried *in vacuo*. In this way 17 grams of pure orthobrombenzylbromide were obtained from 18 grams of orthobromtoluole.

Its purity was established by the following bromine determination:

0.5035 gr. of substance gave, after ignition with CaO, 0.7608 gr. of AgBr.

	Required for $C_7H_6Br_2$.	Found.
Bromine	64.0	64.30

A number of bromine determinations made in products from distillation with steam gave invariably results which were below the theory.

Properties.—It forms a pale yellow oil (the color is undoubtedly due to a trace of some impurity), with an agreeable odor, somewhat resembling that of parabrombenzylbromide, and an action on the mucous membrane even more violent than that of the preceding compounds; its boiling point seems to lie between 250° and 260°, but could not be determined with accuracy because it is decomposed with evolution of hydrobromic acid by boiling. A careful study of the action of heat on this and the allied substances is reserved for a future paper. It does not solidify even at —15°, can be distilled with steam, burns with the usual luminous green-bordered flame, and does not mix with water, although it imparts its odor to it, but mixes readily with absolute alcohol, ether, benzole, glacial acetic acid, and carbonic disulphide. It does not seem to be attacked by a mixture of potassic dichromate and dilute sulphuric acid, but the alcohol derived from it is completely destroyed by this oxidizing mixture.

Parachlorbenzylbromide, $C_6H_4ClCH_2Br$, was prepared from parachlortoluole; melting-point, 6.5°; boiling point, 158°–161°: made by the modification of the method of Huebner and Majert, already described in connection with orthobromtoluole (see page 100); crude fuming hydrochloric acid took the place of the hydrobromic acid, and 40 gr. of paratoluidine were used for each operation; the oil, after washing with potassic hydrate, proved on rectification to be almost absolutely pure parachlortoluole, the yield being about 13 gr. It was converted into parachlorbenzylbromide in the way already described;

the product of the reaction deposited crystals on cooling, which were drained, and a fresh crop obtained from the mother-liquor by heating it gently for a few minutes in a watch-glass placed on a sand-bath, and then allowing it to stand for some time. The crystals after pressing between filter paper were purified by crystallization from hot alcohol in corked flasks, as the substance is so volatile that work in open vessels would have been attended with great loss; upon cooling the solution with ice, a little oil separated; and if the liquid was then stirred it immediately became filled with beautiful white needles.

The composition of the parachlorbenzylbromide was established by the following analyses:

0.3399 gr. of the substance gave, after ignition with CaO, 0.5580 gr. AgBr + AgCl.

0.4224 gr. of substance gave 0.6779 gr. AgBr + AgCl.

	Required for C_7H_6ClBr.	Found.	
Chlorine and Bromine	56.20	57.20	55.94

Properties.—By slow evaporation of its alcoholic solution it can be obtained in well-formed colorless prisms, by cooling in radiated bunches of needles often three centimeters long; it has an agreeable aromatic odor, and acts on the mucous membrane more violently than any of the other substances described in this paper; it melts at 48½°, sublimes in oily drops, can be distilled with steam, is very volatile at ordinary temperatures, so that a crystal will evaporate completely if exposed to the air for a few days, and burns with a flame similar to that of the bromine compounds. It is slightly soluble in water, easily soluble in cold, still more so in hot alcohol, and very readily in ether, benzole, carbonic disulphide, and glacial acetic acid. It is attacked with difficulty, if at all, by potassic dichromate and dilute sulphuric acid. This substance was made but not described by Pauly.* It is highly probable, however, that he did not get it free from the ortho compound.

Paraiodbenzylbromide, $C_6H_4ICH_2Br$, was made from paraiodtoluole; melting point, 35°; prepared according to Kœrner†

* Pauly, Ann. der Chemie, 167, 187.

† Kœrner, Bull. Acad. Roy. Belg. [2], 24, p. 157.

by the action of hydriodic acid on the nitrate of diazotoluole, this last being obtained by Victor Meyer's* excellent modification of Griess's reaction. The introduction of the bromine into the side-chain by treating the boiling substance with bromine vapor was much more difficult than in the preceding cases; the precautions to be observed were in general the same as those given under parabrombenzylbromide; but occasionally, in spite of all possible care, a black tarry liquid was the only result of the process. The conditions under which the paraiodbenzylbromide is formed have been carefully studied by Mr. C. F. Mabery, and the results will be published in his paper upon the paraiodbenzyl compounds. It is a very remarkable fact that in several cases, when the paraiodtoluole was not perfectly pure, the liberation of iodine in considerable quantity was observed during the bromiring; but in spite of this, the product contained paraiodbenzylbromide, thus apparently furnishing an exception to the general rule of Beilstein that, in presence of iodine, bromine goes into the benzole ring even at high temperatures. The product of the reaction, if properly managed, solidified on cooling, and was best purified by standing on paper, which sucked out a quantity of black oil, and afterward by repeated crystallizations from boiling alcohol with the assistance of bone-black.

The composition of the paraiodbenzylbromide was determined by the following analyses:

0.3721 gr. of substance yielded 0.3773 gr. CO_2 and 0.0773 gr. of H_2O.

0.1774 gr. of substance gave, according to Carius, 0.1285 gr. of Ag.

0.1971 gr. of substance gave 0.2755 gr. of AgBr + AgI. There were indications in this anaylsis that the oxidation had not been complete.

	Required for C_7H_6IBr.	Found.	
Carbon	28.28	27.66	...
Hydrogen	2.03	2.31	...
Iodine and Bromine	69.69	69.47	68.41
	100.00	99.44	

Properties.— Crystallized from alcohol it forms flattened

* V. Meyer, Ber. d. chem. Gesell., 1875, p. 1074, note.

needles, which usually have a straw-yellow color, but can be obtained white by repeated recrystallization with bone-black It has an aromatic odor, and attacks the mucous membrane much less violently than any of the other substances mentioned in this paper; this, however, is very probably due to the fact that it is not readily volatile at ordinary temperatures: it melts at 78¾°; does not distil with steam or only with great difficulty; sublimes in needles; burns with a luminous green-bordered flame; and is insoluble in water, almost so in cold, much more soluble in hot alcohol, but slightly soluble in glacial acetic acid, freely in ether, benzole, and carbonic disulphide. It is not easily attacked, if at all, by an oxidizing mixture of potassic dichromate and dilute sulphuric acid.

That all the substances mentioned in this paper contain bromine in the side-chain is proved by the fact that, when boiled with alcoholic sodic acetate, each one of them yields the corresponding substituted benzylacetate, from which the alcohol can be obtained by heating with aqueous ammonia at 150° to 160°. The description of these compounds, as well as of certain other derivatives of these substances, will be found in the following articles of this series.

In closing this paper I am very glad to have an opportunity of thanking Mr. A. W. Field for the intelligent and skillful assistance which he has given me in the preparation of these substances.

AN APPARATUS FOR GAS ANALYSIS FROM SIMPLE LABORATORY MATERIAL.

By A. V. E. Young,
Fellow in Chemistry, Johns Hopkins University.

While working in the subject of gas analysis with the simple Bunsen apparatus, none of the more complicated forms being available, the desirability of effecting economy in time and labor, and of applying liquid reagents entirely outside of

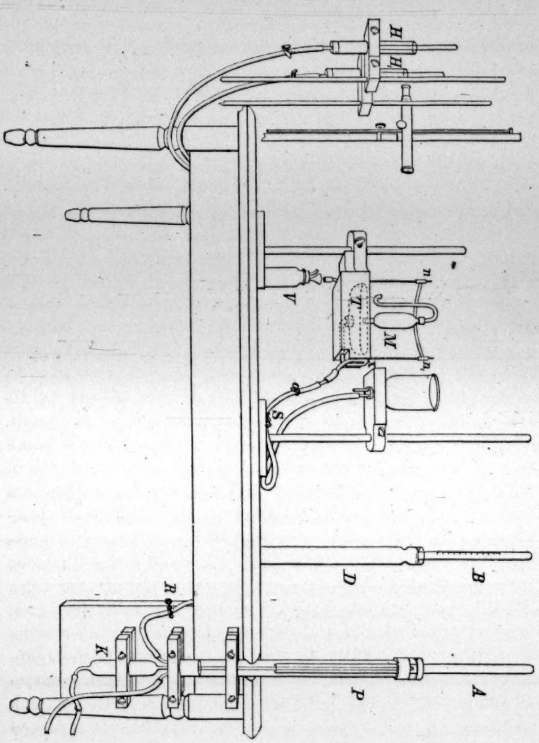
the measuring tube, led me to attempt to realize these results, so far as might be, by some additional apparatus of easy construction and demanding only such material as is usually at hand in a chemical laboratory, or at least easily obtainable. The apparatus thus designed, and now in satisfactory operation, may be described in three parts: 1. The measuring apparatus; 2. The transferring pipette; and 3. The absorption or laboratory vessel.

For the purposes of measurement and explosion the ordinary Bunsen's eudiometer is used, with the platinum wires and millimeter scale, and calibrated as described in Bunsen's "Gasometrische Methoden." To avoid the necessity of barometric and thermometric reductions, the principle of measurement by comparison with a standard volume of air, as described by Williamson and Russel*, is used; but the means employed are different. Instead of raising and lowering the pressure-tube and eudiometer in the same mercury-trough, each tube is supported by an ordinary retort-stand in its own well and remains stationary, while the surface of the mercury is raised or lowered to bring the gases to the desired volume. For pressure-tube a second eudiometer (*B*, *Fig.*) is used. As cistern for this, a student-lamp chimney (*D*), closed at its smaller and lower end by a rubber stopper, serves very well. In order to raise or lower the surface of mercury a small glass tube passes through this stopper and through the top of the work-table, and connects by means of small rubber and glass tubing running underneath the table with a small cylinder and piston (*H*). The cylinder is made of a piece of glass tubing 120 mm. long and 33 mm. in diameter, closed at one end by a cork, through which passes the connecting tube. The piston consists of a cork on the end of a stout glass rod, and fits the cylinder with sufficient closeness to effect the depression and retention of the surface of mercury in the cylinder below the level of that in the cistern, which is in communication with it. The cylinder is supported in a common wooden clamp, which slides up and down upon a rod placed near the telescope, so that the piston can be conveniently raised or lowered by the right hand while the eye is at the telescope. The latter is placed at one end of the work-table

* Proc. Roy. Soc. vol. ix. p. 218.

and the pressure-tube stands near the opposite end, the distance between them being about 2 meters.*

To put in order the pressure-tube, the cistern, cylinder and connecting tubes are filled with mercury, care being taken



that no bubbles of air are retained. The pressure-tube is then partly filled, a convenient volume of air being retained, the

* In the figure the pressure-tube *B* is somewhat displaced from its true position in order to bring it into clearer view. It should stand at the same distance from the telescope as the eudiometer *A*.

saturation of which with aqueous vapor is insured by moistening the walls of the tube before filling. The tube is then inverted and transferred to the mouth of the cistern by means of the shallow spoon used for such purposes; then fixed in a retort-stand in such a position that the enclosed air has a convenient volume, say 300 on the millimeter scale, and the level of the mercury in the tube is from 30 to 60 mm. above that in the outer vessel. Now if the enclosed air undergoes change of volume, it is brought back to its initial volume by means of the piston while the top of the mercury column is watched through the telescope.

To effect the application of liquid reagents outside of the measuring tube, the gas is first withdrawn from the eudiometer by means of the transferring apparatus, which also serves as cistern for it in the operation of measuring. This is simply a stationary pipette (*P*), large enough to receive within itself the eudiometer. It is made of a piece of glass tubing 545 mm. long and 33 mm. diameter, to the end of which is attached, by means of rubber packing and sealing-wax, a short tube of larger diameter, in order merely to make a mouth large enough to receive the eudiometer with its transferring spoon. An argand chimney 50 mm. in diameter was used for this purpose, the two when joined making a cylinder 610 mm. long. The bottom of this is tightly and firmly closed by a rubber stopper, through which pass three small glass tubes (*a*, *b*, *c*). The stopper is forced as far as possible into the tube, and the latter then heated until the rubber softens and adheres closely to the glass. One of the three tubes mentioned (*b*) is 615 mm. long and about 3 mm. interior diameter. It passes through the cylinder, axially, to within 28 mm. of the mouth. It is slightly drawn out at its upper end and the end well rounded. The second tube (*a*) merely passes through the stopper, and makes connection by means of rubber and glass tubing with the cylinder and piston, *H*, similar to the one already described. The third tube, *c*, communicates by a rubber tube with a mercury reservoir (not shown in the figure). The reservoir is held in a wooden clamp which slides up and down upon a post rising from the floor close to the table. The long tube, *b*, is connected by means of a piece of rubber tube only just long

enough to hold a screw clip, with one end of a glass bulb, *K*, 140 mm. long, 38 mm. diameter, the other end of which communicates with a second and smaller mercury reservoir supported like the first. All the rubber tubing used in the apparatus is stout and thick walled, measuring 12 mm. external and 4 mm. internal diameter. For reservoirs, inverted bell-jars answer the purpose, or, still better for the larger one, a druggist's percolator. The connection between the long pipette tube and the bulb below must be made with sufficient care to prevent leakage of gas even under considerable pressure, and also to make a clear channel from which all of the gas shall be expelled by the rise of mercury. Screw clips are placed on the rubber connecting tubes. The figure makes the position and support of the pipette sufficiently clear.

To prepare it for use, mercury is poured into the reservoirs and carefully allowed to fill the rubber tubes so as to expel all the air from them; then, by raising the smaller reservoir, mercury rises in the bulb and long axial tube, completely filling them, and the screw clip at the bulb is then closed. The cylinder of the pipette is then filled from the larger reservoir until the mercury rises a few mm. above the end of the axial tube. The whole is now ready for use, either in the measurement or transference of a volume of gas. For the first operation the eudiometer containing the gas is transferred to the mouth of the pipette, and there is sustained by the left hand while the right controls the level of mercury in the pipette by movements of the reservoir. It is thus lowered over the end of the axial tube until the mercury column sustained within it, read upon its millimeter scale, is a little longer than that in the pressure-tube, the air in the latter being at the initial volume 300. In this position it is fixed perpendicularly in the retort-stand, the clip upon the tube leading to the reservoir is closed, and that (*R*) upon the tube leading to the piston is opened. Now taking position at the telescope, the column in the pressure-tube is brought accurately to the division 300, the reading in the outer vessel giving, say, 350, that is, a column 50 mm. long. A slight turn of the telescope brings the eudiometer into view. The column in this, being, as mentioned above, longer than that in the pressure-tube, is shortened by pressure upon the piston until

it too is 50 mm. long. Now take the reading at the top of the column, and reference to the table of capacity gives the proper volume, provided the two tubes are in the same condition of temperature and atmospheric pressure and the gas in each is saturated with aqueous vapor.

To secure the first two conditions the tubes are not surrounded with water as in many forms of apparatus; but the readings are so easily made, involving no reductions, that it is a simple matter to take a sufficient number to show when they become constant. Ten or fifteen minutes usually suffice for this, if in handling the eudiometer its direct contact with the hand be avoided as much as possible. The apparatus permits an easy adjustment of the mercury levels, since a very considerable movement of the pistons produces but a slight movement of the columns. The final adjustment should always be made by a depression of the piston, that is, by forcing up the mercury column in the tube so that the curve of the meniscus may be always the same.

To effect the transfer of gas from the eudiometer, free the latter from its stand and lower it until its top rests upon the end of the axial tube of the pipette. Then lower the small mercury reservoir and open the clip at the bulb. The mercury sinks in the axial tube, and the gas follows it into the bulb below; meanwhile the mercury rises in the eudiometer until it is completely filled, the last bubble of gas being detached from the platinum wires by jarring the tube against the wall of the pipette. The mercury then flows into the axial tube and the clip at the bulb is quickly closed. The eudiometer is now withdrawn completely filled with mercury, and set aside until again needed. The rest of the operation is simply the reversal of this. The vessel to receive the gas is filled with mercury, transferred to the pipette, lowered over the end of the axial tube, the small reservoir raised and the clip at the bulb slowly and carefully opened. The gas then passes back to the receiver, followed by the mercury. When this flows from the axial tube the bulb-clip is closed and the transfer completed.

Next comes the operation of absorption. For this purpose it was first thought to use a straight tube like the eudiometer, but this was not found practicable. A very convenient and

satisfactory absorption vessel, *M*, is made from a large test-tube, about 180 mm. long and 30 mm. in diameter, by drawing out its bottom to a tube and cutting off the end so as to give an orifice about 1 mm. in diameter, and also drawing together somewhat the open mouth of the test-tube until it becomes about 18 mm. in diameter, so that it can be contained in the transferring spoon used with the eudiometer. To the small end is attached by a bit of rubber tubing 18 mm. long a delivery tube of about 3 mm. bore, which rises a few millimeters above the rubber joint, and then is bent so as to descend parallel and near to the sides of the test-tube to the level of its mouth, and then turns slightly upwards. The inside of the rubber tube making the joint is carefully coated with paraffin to protect it against the reagents, and the delivery-tube is thrust into it somewhat warm, so as to make a gas-tight and at the same time a smooth channel from which all the gas shall be expelled by the rise of mercury within. This furnishes an absorption vessel without the use of any stop-cock, not fragile, and, even if broken, very easily replaced. It is found convenient to have several on hand, varying somewhat in capacity, so as to economize the mercury required to fill them.

In order to manipulate the gas contained in the absorption vessel, a small mercury tank, *T*, is provided, made very simply from a block of wood, and arranged to slide up and down upon a rod as shown in the figure. Its inner dimensions are, length 120 mm., width 55 mm., depth 25 mm. Through its bottom is cut a hole 45 mm. in diameter, and into this from the inner side is firmly pressed a rubber stopper, *m*. This is also pierced by an opening of such diameter (15 mm.) that when the mouth of the absorption vessel is pressed down into it, a joint is made sufficiently close to hold mercury. The opening of the stopper is closed from below by the end of a piece of glass tubing which is attached to the bottom of the tank to prevent strain upon it.* The other end of the glass tube leads by a rubber connection to a small reservoir, which like the others can be raised and lowered. The tank is fixed in a position about 225 mm. above the table, and the rubber tube descends from it to the table and passes under a short

*A bend was made in the tube, as shown at *x*, but was found to be unnecessary.

iron rod at *S*, (a similar one is shown at *R*), hinged at one end so that the other end can be pressed down upon the tube as it lies on the table and thus instantly close it. The rubber stopper is covered by the mercury in the tank to the depth of about 15 mm., so that when the mouth of the absorption vessel is pressed down into its rubber socket, both it and the end of the delivery-tube are completely under mercury. If now the reservoir be raised above the level of the tank and clamped there, and the communicating tube be opened by raising the lever at *S*, the mercury rises in the absorption vessel to its top and then passes down the delivery-tube, thus completely filling the vessel. By allowing it to flow for a few seconds, and then lowering the reservoir and reversing the flow, one can assure himself that no bubbles of gas are retained. By the lever at *S*, the flow of mercury can be perfectly regulated or instantly arrested at any point in the absorption vessel, or even in its descent through the delivery-tube. The tank is provided with an overflow tube which leads to any convenient vessel, *V*; also with a little wire frame, sufficiently shown in the figure at *n* and *n*, for the purpose of holding the absorption vessel erect when filled with mercury.

The operation of absorption, then, would be as follows, supposing the gas already measured and drawn into the pipette bulb: Two absorption vessels having been filled as described, one is set aside; into the other is injected the proper reagent, its delivery-tube having been first closed with a little plug of wood to hold the mercury column in position. It is then transferred to the pipette and lowered over the end of the axial tube until it rests upon the shoulder formed where the pipette cylinder joins the wider tube which forms its mouth. The delivery-tube need not enter the pipette at all. The gas is then allowed to pass in from the bulb, one bubble at a time if so desired. As the mercury is displaced it leaves the wall of the absorption vessel moistened with the reagent, thus exposing a large surface to the gas. When all the gas has passed, and the mercury has flowed for a few seconds, the bulb-clip is closed, and the absorption vessel transferred back to its socket in the tank. Here, by shaking it from side to side, and by letting a stream of mercury flow in through the

delivery-tube, considerable agitation of the gas and reagent can be effected. To recover the gas from the reagent, the second absorption vessel is lowered over the delivery-tube of the first, and held by the left hand while the right regulates the flow of mercury from the reservoir. The gas is thus passed into the second vessel, leaving most of the reagent, perhaps all, in the first. It is hardly safe, however, to attempt to pass it directly from the first into the eudiometer, unless the quantity of reagent used is very small. The second absorption vessel is then pressed into the socket, the filled eudiometer placed over its delivery-tube and the gas passed as before, now free from reagent and ready for measurement. If the mercury column in descending the delivery-tube of the second vessel still bears some of the reagent upon its surface, its motion is arrested at about the middle of the tube and the tube sharply tapped, when the liquid will be drawn up leaving the mercury clean. If a second reagent must be used to absorb vapors from the first, it is injected into the second vessel, and thus cannot interfere with the action of the absorbent proper.

This absorption vessel can also be conveniently employed as collecting vessel in the volumetric estimation of nitrogen and other gases, when separation of gas from liquid is to be accomplished. It is also applicable in the use of reagents which attack mercury, as in the processes described by Berthelot* for the use of nitric acid and bromine to determine benzol vapors, &c. After the absorption is completed as there described, the gas is passed under water from the flask or tube where the reaction takes place to the absorption vessel, previously filled with water. This is then transferred to its socket, and the gas freed from water as already explained.

Although the description here given is of the apparatus actually in use, it will be seen that the latter readily admits of such modifications in dimensions and disposition of parts as surrounding circumstances may suggest.

As indicating the possibility of accurate work with the apparatus are given the following results of two successive determinations of the oxygen in air by absorption with potassic pyrogallate:

* Ann. Chim. Phys. (5) xii.

	First.	Second.
Air taken	197.23	207.20
After absorption	156.07	164.04
Oxygen	41.16	43.16

Oxygen in 100 of air ... 20.87
" " " ... 20.83

Bunsen gives 20.86 per cent. obtained with the same reagent and his absorption balls. The analysis of air can be made in about three-quarters of an hour.

ON THE OXIDATION OF SUBSTITUTION PRODUCTS OF AROMATIC HYDROCARBONS.

II.—ON THE OXIDATION OF XYLENESULPHAMIDES.

By Ira Remsen and M. W. Iles.

(Continued from p. 51.)

Orthocresole from Oxytoluic Acid.

Oxytoluic acid was intimately mixed with quick-lime in the proportion of one part of the former to one and a half parts of the latter. The mixture was distilled and an oil passed over, the main portion of which boiled between 180–190°. It had the characteristic odor of phenoles, and was colored brownish red. It was treated with calcium chloride, and then cooled down by means of a freezing mixture of ice and salt. The entire mass solidified. At the time this experiment was performed orthocresole was known only as a liquid which would not solidify in a freezing mixture. We showed, however, that the cresole in our hands was really orthocresole, and hence we must have obtained it in purer condition than it had hitherto been obtained. Subsequently Tiemann and Schotten* showed that pure orthocresole does solidify easily.

* Ber. d. chem. Gesell., 11, 767.

The cresole prepared in the experiment just described was treated with benzoylchloride, and the benzoyl-compound thus readily obtained. This made its appearance in the form of a light yellow oily liquid, which did not solidify in a freezing mixture. It corresponded closely in its properties to benzoyl-orthocresole described by Engelhardt and Latschinoff.*

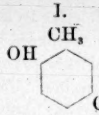
The most positive proof of the nature of this cresole was furnished by fusing it with potassium hydroxide. The substance was kept in contact with the fusing mass for about three hours, the temperature being kept comparatively low. At the end of this time, or when the oil drops had all disappeared, the whole was dissolved in water, acidified with hydrochloric acid and extracted with ether. The ethereal solution left behind, after evaporation, a white crystalline body. On crystallizing this body from water, long, delicate needles, resembling salicylic acid, were obtained in pure condition. The solution gave a violet color with ferric chloride. The substance was volatile with water vapor. The dried needles fused at 154.5°–155°. These properties suffice to show beyond a doubt that our product is salicylic acid. But not a trace of any other product could be found. Hence we are justified in concluding that the cresole obtained from our oxytoluic acid is pure ortho-cresole.

Another experiment was now performed, the result of which served to confirm the result of the experiment just described. A small quantity of the acid was heated in a sealed tube with concentrated hydrochloric acid at 180°–185° for about half an hour. The solution had a slightly reddish color, and a little free carbon was present. The acid solution was partially neutralized with caustic soda, and then extracted with ether. A reddish oil was obtained, and this fused with caustic potassa. In about two hours the operation was completed. On treating the mass in the usual manner a solid, white, crystallized body was obtained by evaporating the ethereal solution. This possessed all the properties of salicylic acid. It crystallized in long delicate needles from water. Its aqueous solution was colored violet by ferric chloride. It fused exactly at 155°. No other substance was formed, so that here again we have good grounds for concluding that the cresole obtained from the oxytoluic acid is only orthocresole.

* Zeitschr. Chemie, N. F. 5, 621.

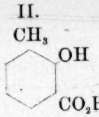
As the hydroxyl group is thus shown to be in the ortho-position with reference to the methyl-group in the oxytoluic acid, the latter may have one of two formulas. It may be either

I.

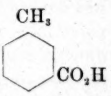


or

II.

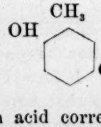


Between these two formulas it would be impossible for us to decide without the aid of further experiments. These were performed and will be described below; but in the meantime an article by Tiemann and Schotten* appeared, in which the same oxytoluic acid is described as that which we are considering. These chemists, however, obtained their acid in an entirely different way, and as they were led to accept the formula which we had already accepted, the probability of the correctness of the conclusion is doubly strong. Tiemann and Schotten started with orthocresole. On treating this with potassium hydroxide and chloroform, according to the now well-known reaction of Tiemann and Reimer, they obtained the aldehydes of two oxytoluic acids, one of which they call orthohomoparaoxybenzoic acid. They conclude that the formula of this acid is



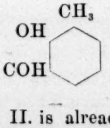
The conclusion is based upon a large number of experiments performed by Tiemann and his associates which show that when the aldehyde group is introduced into a phenole, it takes either the para- or the ortho-position with reference to the hydroxyl. Accordingly an aldehyde obtained from ortho-cresole by this reaction would be either

I.



or

II.



,

but an acid corresponding to formula II. is already known,

* Ber. d. chem. Gesell., 11, 767.

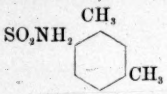
and this is not identical with orthohomoparaoxybenzoic acid. Hence formula I. must be the correct one.

The properties of orthohomoparaoxybenzoic acid agree in most respects with those of our oxytoluic acid; and though the account of the acid given by Tiemann and Schotten is very meagre, probably because it was obtained only in small quantity, still there seems to be no good ground to doubt that the two are identical. Their acid fuses at 172°–173°, after being dried at 100°. Under the same conditions our acid fuses at 174°–175° (corrected). Both acids contain half a molecule of water of crystallization. Both conduct themselves toward chloroform, alcohol, ether and water in the same way. Ferric chloride colors neither one in aqueous solution. While our acid, however, crystallizes in long, delicate, lustrous needles of great beauty, orthohomoparaoxybenzoic acid is described as crystallizing "in kleinen, meist schwach fleischroth gefærbten Nadeln." The difference is probably due to a difference in the degree of purity in which the two substances were prepared. Our acid was undoubtedly perfectly pure, while that of Tiemann and Schotten could not have been so.

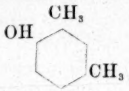
Again it is interesting to note that Jacobsen* has succeeded in obtaining another oxytoluic acid from the same xylenesulphamide with which we started, *i. e.* the *a*-amide of fusing point 137°. He fused the amide directly with potassium hydroxide, and thus obtained, as his first product, the corresponding xylenole. On then further fusing this xylenole with potassium hydroxide, it was first converted into an oxytoluic acid. This acid is not identical with ours, as Jacobsen's description plainly shows. It does not contain water of crystallization. It fuses at 149° (uncorr.). Its solution is colored deep violet by ferric chloride. Its barium salt contains two molecules of water of crystallization, while that described by us contains three molecules of water. The copper salt could not be prepared in good condition, while the copper salt of our acid is very characteristic. The acid of Jacobsen further presents a peculiarity which ours does not present. When distilled with lime it yields orthocresole, as ours does; but when heated in a sealed tube with concentrated hydrochloric acid at 180–185°, it is split up into carbon dioxide and *paracresole*. Our acid, as was

* Ber. d. chem. Gesell., 11, 374.

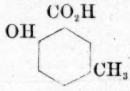
fully described above, yields orthocresole under the influence of both these reagents. Jacobsen regards the experiment with hydrochloric acid as reliable, and considers his acid a derivative of paracresole. The transformations effected by Jacobsen may be represented thus:



Xylenesulphamide, fusing point 137.5°–138°.

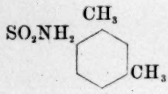


Metaxylenole.

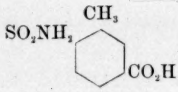


Oxytoluic acid.

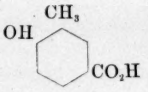
The transformations described by us may be represented thus:



Xylenesulphamide.



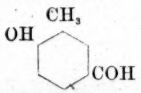
Sulphaminemetatoluic acid.



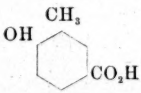
Oxytoluic acid.

Finally, the transformations described by Tiemann and Schotten may be represented thus:

Orthocresole.



Orthohomoparaoxybenzaldehyde.



Orthohomoparaoxybenzoic acid.

We hope to be able to subject homoparaoxybenzoic acid to an exhaustive examination, as we can easily prepare it in large quantity.

It will be seen, on comparing Jacobsen's transformations with ours, that while the sulphamine group evidently protects the ortho-methyl group when the oxidation takes place in acid solution, the hydroxyl group does not protect the ortho-methyl group when the oxidation takes place in alkaline solution. On the contrary, in the latter case the ortho-methyl is first oxidized. Some other observations have been made since these experiments were performed which seem to indicate that it is a general principle, that when oxidation is effected

by means of fusing potassium hydroxide, the ortho-methyl is first oxidized. In another part of this memoir these relations will be considered more fully with reference to their bearing upon the structure of some mesitylene derivatives.

From a consideration then of the results of the experiments just described, we are led to the conclusion, that in our oxytoluic acid the hydroxyl group occupies the ortho-position with reference to the methyl, and the para-position with reference to the carboxyl. Accordingly in sulphaminemetatoluic acid the sulphamine group probably occupies the same relative position. This, however, does not necessarily follow, as the transformations effected by means of fusing potassium hydroxide have, as is well known, been shown to be unreliable. It was hence considered necessary to furnish further proofs of the structure of the acid.

Xylidinic Acid.

If the sulphamine group in sulphaminemetatoluic acid could be converted into carboxyl, the product ought to be xylidinic acid, provided our notions concerning the structure of xylidinic acid and of the sulphamine acid are correct. As the sulphamine group can be so readily transformed into hydroxyl, it was thought that possibly the fusion of the sulphamine acid with sodium formate might also give good results.

Pure, dry potassium sulphaminemetatoluate was intimately mixed with an equal volume of sodium formate, and the mixture heated in a silver crucible. The fusion was performed at as low a temperature as possible. The phenomena which usually accompany this reaction were observed. The mass became black, and inflammable gases escaped from the mouth of the crucible, and these had the offensive odor characteristic of organic sulphur compounds. After cooling, the mass was dissolved in water, filtered, made ammoniacal and boiled with animal charcoal. Hydrochloric acid was added to the filtrate, and a precipitate with a yellow color obtained. This product was still quite impure. It was dissolved in a small quantity of alcohol, the solution filtered, and then a considerable quantity of water added. By repeating this process a few times a comparatively pure product was obtained, though it was found

to be very difficult to thoroughly purify the acid. It retained to the last a yellow tint. A small portion was sublimed, and was thus deposited in the form of short thick needles. These fused between 280°–282.5° (uncorr.). We examined a small specimen of xylidinic acid in our possession, and found that the two acids fused at exactly the same point. The acid obtained by us was extremely difficultly soluble in water, hot as well as cold. This fact also is in accordance with the supposition that we actually have to deal with xylidinic acid.

A portion of the acid was first neutralized with ammonia, and a solution of zinc sulphate added. On boiling this solution the highly characteristic *zinc salt* of xylidinic acid was thrown down, as described by Jacobsen.* The salt was found to be very difficultly soluble in hot water, and comparatively easily in cold water.

The *calcium salt* was prepared by boiling the acid in water with finely powdered Iceland spar. It was obtained in the form of scales. Though recrystallized a number of times, the result of the analysis shows that it was not perfectly pure. Like the free acid, it retained a yellow color to the last.

0.2183 grams dried salt gave 0.1303 grams $CaSO_4$.

	Calculated.		Found.
$C_9H_6O_4$	178	...	...
Ca	40	18.35	17.55

Although the results of the experiment just described are not as satisfactory as could be desired, there can hardly be any doubt that the bibasic acid obtained was really xylidinic acid. Hence we are again led to the formula already accepted for sulphaminemetatoluic acid, and the conclusion drawn is made doubly probable. But the value of the reaction with sodium formate has been doubted as well as that with potassium hydroxide. Though the results reached through it could not then be considered decisive, any more than those reached through the reaction with potassium hydroxide, still when both lead to precisely the same conclusion it is plain that the chances are in favor of this conclusion being correct. We are, however, able to furnish still further proofs of its correctness.

* Ber. d. chem. Gesell., 10, 859.

Sulphoisophthalic Acid.

The oxidizing mixtures from which the main portion of sulphaminemetatoluic acid was obtained were concentrated, and thus a few additional crops of crystals of the acid were obtained. In these new portions no second isomeric acid, except one derived from paraxylene, was discovered, though every precaution was taken against error. This fact again serves to strengthen the opinion expressed above that, if β-xylenesulphamide yields a monobasic acid by oxidation, this acid must be unstable towards the oxidizing mixture employed. Our object in examining the filtrates from the sulphaminemetatoluic acid first obtained was expressly to decide whether or not a second acid was formed. And, although the quantities worked up by us yielded nearly *eighty grams* of perfectly pure sulphaminemetatoluic acid, not an indication of the presence of an isomeric acid, except the one above referred to, was observed. At the same time two new products were obtained from the last mother-liquors, and these proved to be derivatives of bibasic acids.

Both the new products were found to be easily soluble in water, and to fuse at a much higher temperature than sulphaminemetatoluic acid. On purification they were found to crystallize well from water. A more careful examination showed them to be acid potassium salts. The quantities obtained from these mother-liquors were so small that it would have been impossible to determine the nature of the salts had we not soon discovered a method by which they could be prepared in large quantity and perfectly pure.

Suspecting that the salts might be derived from bibasic acids formed by further oxidation of the monobasic sulphaminemetatoluic acid and its isomere from paraxylene, and believing that the oxidation of the second methyl group could probably be more easily effected by means of potassium permanganate, an experiment was at once made with this agent. The result was perfectly satisfactory. It was found that sulphaminemetatoluic acid can be quantitatively converted into a new acid, and that the acid can be easily obtained in the form of its acid potassium salt. This salt is identical with one of those obtained, as above described, from the chromic acid oxi-

dizing mixtures. In the same way subsequent experiments showed that the second salt mentioned above could be readily formed by treating the monobasic acid derived from paraxylene with potassium permanganate. These derivatives from paraxylene will be considered farther on. At present we will confine our attention to the oxidation of sulphaminemetatoluic acid by means of potassium permanganate.

The best conditions for this experiment are, according to our experience, the following: To 1 gram sulphaminemetatoluic acid, take 5 grams potassium permanganate, and dissolve in 100 cc. water. This mixture is heated on a water-bath for about seven hours. At the end of this time a little permanganate still remains unreduced. A few drops of alcohol, or of a solution of sulphur dioxide, are added to effect the reduction, and, when the solution is colorless, it is filtered. The filtrate has a slightly alkaline reaction. It is evaporated down to about one-sixth to one-eighth of its volume, acidified with a little hydrochloric acid, and allowed to stand after filtering. On cooling, a perfectly homogeneous mass of acicular crystals is deposited. After one recrystallization these are, as far as could be determined, perfectly pure. On concentrating the mother-liquor from the first crop of crystals, a second deposit was obtained, and this, purified by recrystallization from water, proved to be identical with the first product. On still further concentrating, more of the substance crystallized out together with potassium chloride, but no other substance could be found. The conclusion is thus justified, that when sulphaminemetatoluic acid is treated with potassium permanganate, under the circumstances just described, it is completely converted into an acid which yields an acid potassium salt. The quantity of the salt obtained was, further, in accordance with this conclusion. The yield was almost quantitative. If any deep decomposition of the acid takes place it is to an exceedingly slight extent.

We naturally suspected that the new acid was sulphamineisophthalic acid, produced by the oxidation of the second methyl group still contained in the monobasic acid, and the results of the determination of the amounts of potassium and sulphur contained in the salt confirmed this supposition. Nevertheless, on attempting to determine the amount of nitro-

gen in the salt we were surprised to find that none was present. On now testing for the presence of nitrogen by fusing a little of the salt with sodium and then testing for cyanogen, not a trace of nitrogen could be discovered. These tests were repeated very frequently, the greatest care being always taken, but the result was always the same. The oxidizing process has hence undoubtedly removed the nitrogen from the original substance. What acid could now have been formed from sulphaminemetatoluic acid containing no nitrogen but containing the same, or nearly the same, amount of potassium and of sulphur in its acid potassium salt? The molecular weight of sulphamineisophthalic acid is 245, while that of sulphoisophthalic acid is 246. A difference of only 1 in the molecular weights of substances as complex as these could not possibly be detected by means of our ordinary analyses. It, hence, seemed very probable that we had sulphoisophthalic acid before us, and this was afterwards shown to be the case. The results of the analyses of the potassium salt were as follows:

I. 0.257 grams salt lost 0.02875 grams H_2O at 190°; and gave 0.07025 grams K_2SO_4.

II. 0.3461 grams salt lost 0.03925 grams H_2O at 190°; and gave 0.0931 grams K_2SO_4.

III. 0.3931 grams salt lost 0.0446 grams H_2O at 130°; and gave 0.1053 grams K_2SO_4.

IV. 0.340 grams salt gave 0.24222 grams $BaSO_4$ when oxidized by fusion with caustic potassa and treatment with bromine water.

	Calculated.		Found.			
			I.	II.	III.	IV.
$C_8H_5O^7$	213	66.54	..	..	..	..
S	32	10.00	..	..	..	9.78
K	39.1	12.21	12.27	12.07	12.03	..
$2H_2O$	36	11.25	11.19	11.34	11.35	..
	320.1	100.00				

The salt is the *monopotassium salt of sulphoisophthalic acid.* While, from the absence of nitrogen, the substance can not, of course, be a derivative of sulphaminemetatoluic acid, it is interesting to notice how easily the results of the analyses of the

salts might deceive the experimenter in regard to the nature of the acid. It is a growing custom among chemists to rely upon determinations of the amount of metal and water of crystallization in a salt for information in regard to the composition of the acid. There are many cases, it is true, in which the complete analysis of salts seems to be superfluous. On the other hand, that there is danger in the usual method is indicated clearly by the example with which we are dealing; and it is certainly better to do some apparently superfluous work than to draw a radically wrong conclusion for want of this work. We speak feelingly upon this subject, for we were ourselves at first deceived; and, our erroneous impressions having been communicated in a short notice* published in Germany a few month ago, Jacobsen was apparently misled by it; and, although we have corrected our first statement, Jacobsen still clings to the error with considerable tenacity. Indeed he goes so far as to assert† that "eine andere Sæure (als die Sulfaminisophtalsæure) bildet sich ueberhaupt nicht bei der Oxydation des *a*-Metaxylolsulfamids oder der zunæchst daraus entstandenen Sulfamintoluylsæure."

Whatever Jacobsen may have obtained in the course of his experiments by the oxidation of *a*-xylenesulphamide, or of sulphaminemetatoluic acid, it is certain that his broad assertion is not true. It is difficult to understand why he should have obtained only one product, and we also only one, and the two should not be identical. As far as it is possible to judge from his descriptions of his experiments, we worked under essentially the same conditions. Nevertheless he asserts positively that his product is sulphamineisophthalic acid, and that no other product is formed. He gives an analysis which was made to determine the amount of nitrogen in his compound, and the results agree closely with those required by the formula.

In view of this very marked disagreement in our results, a very careful special series of experiments was undertaken by us to enable us to come to a final conclusion upon the subject. As the principal result, we may say here *that there can not be the slightest doubt that the substance obtained by us is in reality sulphoisophthalic acid, and we have not succeeded in making sulphamineisophthalic acid up to the present.*

* Ber. d. chem. Gesell., 11, 1336. † Ibid. 11, 1529.

If the acid potassium salt obtained by us is a salt of sulphoisophthalic acid, then, as it contains but one atom of potassium in the molecule, there must still be two acid hydrogen atoms in each molecule of the salt. Whereas, plainly, if the salt is derived from sulphamineisophthalic acid, then there can only be one acid hydrogen atom in each molecule. Of course it is a very simple matter to decide between these two very different cases. It is only necessary to neutralize a weighed portion of the salt with a solution of an alkali of known strength. For this purpose a solution of ammonia ($\frac{1}{10}$ normal) was used, and the results obtained are here detailed:

I. 0.1909 grams salt were titrated with the ammonia solution. There were used for neutralization 12 ccm., whereas 11.9 ccm. were required according to the theory.

II. 0.17975 grams salt required 11.3 ccm. of the solution of ammonia, while the theoretical amount is 11.2 ccm.

III. 0.8338 grams salt required 52 ccm. of the solution of ammonia, while the calculated quantity is 52.12 ccm.

These results permit only one conclusion. The acid from which the potassium salt is derived is *tribasic;* and, hence, can not be sulphamineisophthalic acid. Taking this fact together with those already stated, it is perfectly clear that our new acid can only be *sulphoisophthalic acid.*

An objection might be made to our mode of experimenting. It might be thought possible that sulphamineisophthalic acid is actually formed at first, and that this is then converted into the sulpho-acid by evaporation in the alkaline solution. This seemed very improbable, as the solution was but very slightly alkaline. Then, too, Jacobsen worked just as we did, and yet, according to his statement, he obtained the sulphamine acid. Still we performed the experiment in such a way as to entirely meet the possible objection. Instead of adding the hydrochloric acid to the solution after evaporation, it was added immediately after the oxidation was finished, and the acid solution then evaporated. The product obtained contains no nitrogen, and is absolutely identical with the acid potassium salt already described.

If the attempt is made to explain the anomalies between the results obtained by Jacobsen and those obtained by us, embarrassment is the immediate result. It is very noteworthy that

the properties of the compound which Jacobsen considers to be sulphamineisophthalic acid, and of that one which, according to our experiments, is, beyond a doubt, sulphoisophthalic acid, are almost identical. They agree so closely that even Jacobsen assumes* that we had the same acid that he had, and "allem Anscheine nach in reinem Zustande." In the description of the acid and its salts to be given below we shall call particular attention to these marked resemblances. Here it is sufficient to refer to the acid potassium salts of the two acids. The description given by Jacobsen for his acid potassium sulphamineisophthalate is almost word for word the same as our description of acid potassium sulphoisophthalate.

We have begun the study of sulphoisophthalic acid and its derivatives, and give here the results thus far reached.

Monohydro-barium Sulphoisophthalate.

$C_6H_3\begin{Bmatrix} SO_3O \\ COO \\ COOH \end{Bmatrix} Ba + 1\frac{1}{2}H_2O.$ When barium chloride is added to a solution of the acid potassium salt, no change takes place in the cold. But on heating the solution a very difficultly soluble, crystalline barium salt is precipitated. As soon as it begins to appear, the contents of the vessel begin to bump so violently that they are thrown out, unless precautions are taken to prevent this result. This bumping is apparently characteristic of the barium salt; at least we have observed it in every preparation. The salt was collected, dried in the air and analyzed.

I. 0.2986 grams salt lost 0.0201 grams H_2O at 200°, and gave 0.16885 grams $BaSO_4$.

II. 0.21125 grams salt lost 0.0135 grams H_2O at 210°, and gave 0.1195 grams $BaSO_4$.

III. 0.2485 grams salt lost 0.01675 grams H_2O at 210°, and gave 0.141 grams $BaSO_4$.

IV. 0.2226 grams salt lost 0.0146 grams H_2O at 210°, and gave 0.1284 grams $BaSO_4$.

* Ber. d. chem. Gesell., 11, 904.

	Calculated.		Found.			
			I.	II.	III.	IV.
$C_6H_4O_7S$	244	59.80	..	..	..	..
Ba	137	33.58	33.25	33.26	33.36	33.92
$1\frac{1}{2}$ H_2O	27	6.62	6.73	6.39	6.74	6.56
	408	100.00				

The formation of the barium salt from the potassium salt takes place according to the equation:

$$C_6H_3\begin{cases}SO_2OK\\COOH\\COOH\end{cases} + BaCl_2 = C_6H_3\begin{cases}SO_2O\\COO\\COOH\end{cases}Ba + KCl + HCl.$$

Hydrochloric must be set free, if this equation expresses what takes place. In order to decide this point the solution from which the barium salt was precipitated was distilled, and the distillate examined for free hydrochloric acid. When the necessary concentration was reached, unmistakable evidence of the presence of the free acid in the distillate was obtained. The experiment was repeatedly performed, and always with the same result.

When this acid barium salt is treated with barium carbonate in water it passes into solution, and the process is accompanied by an evolution of carbon dioxide. This experiment again shows that the acid with which we are dealing is a tribasic acid. The solution containing the neutral barium salt was evaporated, but it was soon seen that the salt was undergoing some decomposition. The liquid became cloudy, and a very difficultly soluble salt was deposited in crusts and as a fine powder. The character of this decomposition we have as yet been unable to investigate, but we hope soon to take up its study.

From the observations made by us we are inclined to the belief that the three acid groups contained in sulphoisophthalic acid have different strengths. It is, of course, probable that the sulpho-group is stronger than the two carboxyl groups, but it also seems as though these two groups differ from each other. The observations bearing upon this point are as yet very imperfect, and they are only mentioned here to indicate a direction in which the study of this tribasic acid, as well as

another which has been prepared and is now being studied in this laboratory, will be taken up. If acetic acid is added to a solution of the neutral barium salt, the acid barium salt described above is precipitated, thus showing that acetic acid is stronger than one of the acid groups. If now hydrochloric acid be added to the difficultly soluble barium salt it is easily dissolved, showing that it is, at least partially, decomposed. It may be that the acid salt is completely decomposed by hydrochloric acid, yielding free sulphoisophthalic acid, but in view of the great stability of the acid potassium salt, to be considered below, this does not seem probable. It hence appears that in sulphoisophthalic acid one carboxyl is weaker than acetic acid, and one stronger, while they are both weaker than hydrochloric acid. It would, of course, be interesting to determine which of the carboxyl groups is the stronger, and attempts will be made to gain light upon this point. In general the study of the relations of different acid groups in the same molecule promises interesting results, and attention has already been turned to this field in our laboratory.

We have above called attention to the marked similarity between Jacobsen's description of the acid potassium salt of his sulphamineisophthalic acid and our description of the corresponding salt of sulphoisophthalic acid. As regards the barium salt, Jacobsen says:* "Aus der Lœsung (des sauren Kaliumsalzes) fællt Chlorbarium ein fast unlœsliches, beim Kochen dichter und krystallinisch werdendes Bariumsalz." That is exactly what takes place in the case of sulphoisophthalic acid. As Jacobsen gives no analyses of the salt prepared by him, a close comparison of the two is impossible.

Monohydro-calcium Sulphoisophthalate.

$C_6H_3\begin{Bmatrix} SO_2O \\ COO \\ COOH \end{Bmatrix} Ca + 4\frac{1}{2}H_2O.$ This salt was prepared by treating the free acid with Iceland spar. It is probable that in the process of concentration, decomposition of the neutral salt first formed takes place, as noticed in the case of the neutral barium salt. The final solution, from which the salt

* Ber. d. chem. Gesell., 11, 900.

here described was obtained, had been frequently filtered before it could be obtained clear. A closer study of the salt will show whether the supposition is correct. A somewhat similar case is presented by sulphoterephthalic acid, prepared and briefly described by Ascher.* The salt obtained after treating the solution of the sulpho-acid with an excess of barium carbonate has the formula $\left(C_6H_3\begin{cases}(CO_2H)_2\\SO_3\end{cases}\right)_2 Ba$.

The calcium salt under consideration is very easily soluble in water, and crystallizes in compact, apparently monoclinic prisms. The crystals lose part of their water of crystallization when exposed to the air.

The salt was analyzed with the following results:

I. 0.48475 grams salt lost 0.10875 grams H_2O at 205°, and gave 0.18225 grams $CaSO_4$.

II. 0.2223 grams salt lost 0.0490 grams H_2O at 205°, and gave 0.0840 grams $CaSO_4$.

	Calculated.		Found.	
			I.	II.
$C_8H_4O_7S$	244	66.85	...	...
Ca	40	10.96	11.06	11.11
$4\frac{1}{2}H_2O$	81	22.19	22.43	22.04
	365	100.00		

The *silver salt*, obtained by adding silver nitrate to a solution of one of the neutral salts, is amorphous, and difficultly soluble in water.

Finally, free sulphoisophthalic acid was obtained by treating the acid barium salt with moderately concentrated sulphuric acid. The acid potassium salt is remarkably stable. It can be boiled with strong hydrochloric or sulphuric acid without undergoing decomposition, the salt crystallizing out of the acids on cooling. The free acid, obtained from the barium salt, is easily soluble in water, and crystallizes out of the concentrated solution in the form of short, lustrous needles. It fuses, according to our latest determinations with pure acid, at 285°–287°. In our first notice concerning this acid we gave the fusing-point 282°–284°. Now this is the point afterwards

*Ann. der Chemie, 161, 3.

given by Jacobsen as that at which his sulphamineisophthalic acid fuses, so that here again we have a marked agreement in properties between two substances which are quite unlike in composition. We shall continue the study of sulphoisophthalic acid, and shall hope to hear more concerning sulphamineisophthalic acid from Jacobsen, so that the differences between the two acids may become apparent.

The formation of sulphoisophthalic acid by the action of the chromic acid mixture upon *a*-xylenesulphamide is the first case in which the conversion of an ortho-methyl-group into carboxyl has been effected by the acid oxidizing agent. While this change plainly can be effected, contrary to the usually accepted notions on this subject, it is a significant and important fact that only a very small portion of the bibasic acid is formed, and the oxidation process which produces it must be regarded as altogether secondary to the main reaction. If this action were not secondary, if there were no conditions tending to prevent it, then, with an excess of the oxidizing mixture such as we employed, and long-continued heating, the monobasic acid must inevitably have disappeared, and the main product at least must have been the bibasic acid. But it has been shown that the amount of the monobasic acid obtained was very large, while that of the bibasic acid was comparatively insignificant. Hence it can not be doubted that something exerts a protective influence upon one of the methyl groups, and this we believe to be the negative group which is situated in the ortho-position with reference to the protected methyl. The fact that the protection is not complete is no objection to the view that protection is exerted; nor does it in the least detract from the importance of the general conclusion drawn in regard to the action of negative groups upon hydrocarbon residues in the ortho-position.

The transformation of the sulphamide-group into the sulpho-group by both the oxidizing agents used — chromic acid and potassium permanganate — is curious, and was entirely unexpected. From experiments since made here, it is certain that potassium permanganate does not effect this transformation of the sulphamide-group in all compounds; that in some cases the transformation is complete, while in still others it is only partial. Of course it is too early to offer anything like a final

opinion upon this new set of changes, but from the observations already made it seems probable that only those sulphamide-groups which are situated in the ortho-position with reference to groups undergoing oxidation are changed to the sulpho-group by oxidation. Three well-marked cases have been studied here thus far, and others will soon be taken up, but the consideration of this subject will be postponed until the investigations bearing upon it have been completed, or so far completed as to leave no doubt in regard to the interpretation to be offered.

Transformation of Sulphoisophthalic Acid into Oxyisophthalic Acid (α-Phenoledicarbonic Acid).

The formation of sulphoisophthalic acid by the methods described above does not afford any aid in the solution of the main problem before us, which is the determination of the relative positions of the groups in sulphaminemetatoluic acid. While the experiments thus far discussed make it almost certain that the structure assigned by us to the compound is correct, there remains still another transformation to be described which only serves to confirm the conclusions already drawn. This is the transformation of sulphoisophthalic acid into the corresponding oxy-acid, which proved to be identical with α-phenoledicarbonic acid, first prepared by Ost,* and recently again by Tiemann and Reimer.†

Acid potassium sulphoisophthalate in moist condition was added gradually to fusing potassium hydroxide. The reaction proceeded quietly, and in a few minutes the change was complete. The mass was dissolved in water and hydrochloric acid added in excess. A voluminous precipitate was formed. This was colorless and consisted of very fine short needles. It was recrystallized from water, and, after the first crystallization, it was obtained in perfectly pure, white, delicate, short needles. The yield seemed to be quantitative. After drying, the acid was analyzed:

0.205 grams acid gave 0.064 grams H_2O, and 0.3952 grams CO_2.

* Journ. prak. Chemie, N. F. 14, 93, and 15, 301.
† Ber. d. chem. Gesell., 10, 1571.

		Calculated.		Found.
C_8	...	96	52.75	52.58
H_6	...	6	3.30	3.47
O_5	...	80	43.95	...
		182	100.00	

The analysis shows that the acid has the composition of an oxyphthalic acid.

The aqueous solution of the new acid is colored deep reddish violet by ferric chloride. It is very difficultly soluble in hot water, almost insoluble in cold water; easily soluble in alcohol and ether, insoluble in chloroform, even at the boiling temperature. The acid contains no water of crystallization, and fuses at 298–299° (uncorr.).

But these are the properties given by Ost and by Tiemann and Reimer as characterizing their *a*-phenoledicarbonic acid. The study of the salts of our acid also showed almost perfect agreement with the descriptions given for the salts of *a*-phenoledicarbonic acid.

Barium oxyisophthalate, $C_6H_3.OH.(CO_2)_2Ba$. This salt was made by treating the free acid with pure barium carbonate. It crystallizes in small, compact, radiating needles. It is easily soluble in hot and cold water. The dried salt was analyzed:

I. 0.1515 grams salt gave 0.11075 grams $BaSO_4$.

II. 0.131 grams salt gave 0.0968 grams $BaSO_4$.

		Calculated.		Found.	
				I.	II.
$C_8H_4O_5$	...	180	56.79	...	...
Ba	...	137	43.21	42.98	43.45
		317	100.00		

Calcium oxyisophthalate, $C_6H_3.OH.(CO_2)_2Ca$, was prepared by treating the free acid with finely powdered Iceland spar. It crystallizes in small compact needles, very similar to those of the barium salt, and is, like the barium salt, easily soluble in cold and hot water. The dried salt was analyzed:

I. 0.1147 grams salt gave 0.070 grams $CaSO_4$.

II. 0.07775 grams salt gave 0.0475 grams $CaSO_4$.

		Calculated.		Found.	
				I.	II.
$C_8H_4O_5$	...	180	81.82	...	..
Ca	...	40	18.18	17.95	17.97
		220	100.00		

Cadmium oxyisophthalate, $C_6H_3.OH(CO_2)_2$ Cd. This salt was prepared by adding cadmium nitrate to a solution of the neutral ammonium salt. After a short time it separates in fine, short needles. Its properties agree with those given by Ost. It was analyzed after being allowed to dry in the air:

I. 0.22925 grams salt lost 0.05825 grams H_2O at 160°.

II. 0.25275 grams salt lost 0.0645 grams H_2O at 160°, and gave 0.08325 grams CdO.

		Calculated.		Found.	
				I.	II.
$C_8H_4O_5$	...	180	46.04	...	...
Cd	...	112	28.64	...	28.83
$5\frac{1}{2}H_2O$	...	99	25.32	25.41	25.52
		391	100.00		

Normal silver salt, $C_6H_3.OH\begin{matrix}CO_2Ag\\CO_2Ag\end{matrix}$. This was obtained as an amorphous precipitate on adding silver nitrate to a solution of the neutral ammonium salt. Its properties agreed with those given by Ost for his neutral silver salt. Like the latter, our salt held a small amount of moisture very firmly, and, in order to get it perfectly dry, we heated up to 180° for some time. It contains no water of crystallization.

0.26465 grams salt gave 0.14475 grams Ag.

		Calculated.		Found.
$C_8H_4O_5$	...	180	45.45	...
Ag_2	...	216	54.55	54.69
		396	100.00	

Acid silver salt, $C_6H_3.OH.\begin{matrix}CO_2H\\CO_2Ag\end{matrix}$. According to Ost, if an excess of silver nitrate is added to a solution of free oxyisophthalic acid, the acid silver salt is formed, and separates in the

form of fine needles. We cannot confirm this statement. The experiment was performed repeatedly, and the neutral silver salt obtained in each case. In some experiments the amount of silver contained in the salt obtained was a little less than that required by the neutral salt, but it was never nearly as small as that required for the acid salt. If, on the other hand, acetic acid be added to the solution of the neutral ammonium salt, as recommended by Tiemann and Reimer,* and then an excess of silver nitrate added, the acid silver salt separates readily, and possesses the properties mentioned by Ost and by Tiemann and Reimer. In view of the fact that all other salts of our acid agree closely with the same salts of *α*-phenoledicarbonic acid, it seems at least possible that Ost's observation with reference to the formation of the acid silver salt is not correct. Perhaps his solution of silver nitrate contained a little free nitric acid.

The analysis of the acid silver salt gave the following result:

0.41 grams salt gave 0.1525 grams Ag.

		Calculated.		Found.
$C_8H_5O_5$	...	181	62.63	...
Ag	...	108	37.37	37.20
		289	100.00	

The salt crystallizes in fine needles, which are very difficultly soluble in cold water, and easily soluble in hot water. Further, we applied all the tests which are given by Tiemann and Reimer,† and were unable to detect any difference between our acid and *α*-phenoledicarbonic acid. There can hence be no doubt that our product is the latter acid.

If our views in regard to the structure of sulphaminemetatoluic acid are correct, *α*-phenoledicarbonic acid ought to have one carboxyl group in the ortho-position and the other in the para-position with reference to the hydroxyl group. Its formula may be conveniently represented thus,

But this is the formula accepted by Ost and by Tiemann and Reimer, and they were led to it by entirely differ-

* Ber. d. chem. Gesell., 10, 1574, Tab. II. † Loc. cit. p. 1574, Tab. II.

ent lines of thought. It is unnecessary to recapitulate here in detail the arguments of these chemists in favor of the formula given, but it may be mentioned that Ost succeeded in obtaining from his acid both salicylic and paraoxybenzoic acids. This indicates that the hydroxyl occupies the positions with reference to the two carboxyls which are characteristic of salicylic and paraoxybenzoic acids. And again Tiemann and Reimer made *a*-phenoledicarbonic acid by introducing a carboxyl group into salicylic acid, and also by introducing a carboxyl group into paraoxybenzoic acid, and the conclusion is again forced upon us that in the bibasic acid we have, as it were, a combination of salicylic and paraoxybenzoic acids, a fact which is expressed very clearly by the formula above given.

Conclusion.

Thus our first conception in regard to the nature of sulphaminemetatoluic acid is shown to be correct by a variety of methods of proof; and up to the present not a single fact is known to us which is not in perfect harmony with the conception.

Jacobsen has given other proofs for the structure of the *a*-xylenesulphamide with which we started, and the results of his experiments agree with those performed by us, as far as they bear upon the structure of the amide. His method of work was entirely different from ours. He first converted the amide into the corresponding sulphonic acid, and fused the potassium salt of the acid with potassium cyanide. The cyanide thus obtained was heated with concentrated hydrochloric acid at 180°. Thus an acid was formed which was volatile with water vapor. Another portion of the potassium salt used in the experiment just mentioned was fused with sodium formate, and an acid produced which proved to be identical with the one from the cyanide. The acid thus obtained is xylylic acid. It was further oxidized by means of potassium permanganate yielding xylidinic acid. This transformation shows that *a*-metaxylenesulphamide has the structure which we have already assigned to it on the basis of our experiments.

We have thus proved satisfactorily that when a substance

in which there are present a sulphamide-group and two methyl-groups, the former being in the ortho-position with reference to one methyl and in the para-position with reference to the other methyl, is oxidized by means of potassium pyrochromate and sulphuric acid, the ortho-methyl is almost completely protected from the action of the oxidizing agent, while the para-methyl is easily converted into carboxyl. One step has been taken towards showing what antecedent conditions are common in connection with the phenomena briefly discussed in the introduction to this memoir. But of course it is necessary to show that negative groups in other cases protect hydrocarbon residues in the ortho-position. Since these investigations were begun, some experiments have been performed by other chemists, the results of which are in accordance with our hypothesis; and, though one of us (R) will have occasion to discuss these results hereafter, it may be well at least briefly to refer to them at this point, as they are of the highest importance for us.

E. v. Gerichten has shown* very recently that when a chlorcymene, derived from carvacrole, is oxidized, it yields a chlortoluic acid. Now, in the chlorcymene employed it is known that the chlorine occupies the ortho-position with reference to the methyl, and the meta-position with reference to the propyl. But the propyl group is converted into carboxyl by oxidation, while the methyl is protected—a result which, as will be seen, serves to confirm the hypothesis. Again the same chemist has made an isomeric chlorcymene from thymole, and in this derivative the chlorine occupies the ortho-position with reference to the propyl, and the meta-position with reference to the methyl. On oxidizing this an acid was formed which has the composition of a chlorpropylbenzoic acid. The natural conclusion was that now the propyl had been protected while the methyl had been changed to carboxyl. This should certainly be the true explanation if our hypothesis is correct. In a later publication,† however, v. Gerichten claims that the acid formed by oxidation of the chlorcymene from thymole is not a chlorpropylbenzoic acid, but that it has the composition $C_6H_3.CH_3.Cl.C_3H_4.CO_2H$, according to which it is methylchlorhydrocinnamic acid. If this is true, then, as v.

* Ber. d. chem. Gesell., 11, 364. † Ib. 11, 1719.

Gerichten says, the protection exerted upon the propyl-group by the chlorine in the ortho-position is not complete but only partial. It would, however, be very remarkable to find that a methyl-group in a compound like the chlorcymene of v. Gerichten should resist the action of chromic acid. It will be shown in the course of these investigations that orthomethyl groups, situated exactly like this remarkable one in the molecule, are oxidized with great ease; and, indeed, the experiment of v. Gerichten upon the other chlorcymene shows that a hydrocarbon residue situated in the meta-position with reference to the negative group can be oxidized. Why then, we repeat, should this solitary methyl act so strangely? As v. Gerichten still entertains some doubt concerning the correctness of his conclusion in regard to his last experiment, it may, perhaps, not be going too far if we also reserve our opinion until something more definite is heard about the new methylchlorhydrocinnamic acid. It is possible that it may finally prove to be what it was originally thought to be, viz. chlorpropylbenzoic acid.

Again, Schmitz has just published* the results of an investigation on mesitylene derivatives, and some of these results bear closely upon the question we are discussing. He examines the nitromesitylenic acid formed by oxidation of nitromesitylene, and finds that in it the nitro-group is situated in the ortho-position with reference to both the methyl-groups; a fact which shows that the negative group exerts a protecting influence upon both these methyl-groups. The same fact was proved in connection with brommesitylenic acid obtained by oxidation of brommesitylene; the bromine protects two of the methyl-groups, and the third, being unprotected, is oxidized.

In the parts of these investigations which are still to be presented, other cases similar to the one we have thus far been chiefly occupied with will be considered. In the first portion of this paper we referred to an amide obtained by us from the first crude mixture which we suspected to be a derivative of paraxylene. This was deposited from the last mother-liquors in the form of verrucous masses, and found to fuse at 143°. In order to determine its nature it was first subjected to oxi-

*Ann. der Chemie, 192, 160.

dation and converted into a monobasic acid. This acid, on being heated with concentrated hydrochloric acid up to 220°, was converted into a new substance which crystallized from the liquid on cooling. The crystals were filtered off and recrystallized, and, after drying, they were sublimed. They then fused at 174°. Although paratoluic acid, when perfectly pure, melts at 178°, still the properties of this substance are such as to leave little doubt that it is paratoluic acid. A small quantity of the supposed paratoluic acid was treated with potassium pyrochromate and sulphuric acid. It was thus converted into an acid which is insoluble in water, and did not fuse at 310°. This, in all probability, is terephthalic acid.

We hence conclude that the acid derived from the amide is sulphamineparatoluic acid, and further that the amide is a derivative of paraxylene as we supposed. We prepared more of the new acid and studied some of its salts, but it still remains to decide positively what relation exists between the three groups in the compound. It will probably be shown that the sulphamide group occupies the meta-position with reference to the carboxyl, and the ortho-position with reference to the methyl. The account of the full investigation of this acid will be given later. A method has been discovered by which it can be prepared in almost unlimited quantity, so that the investigation of its relations will be somewhat exhaustive.

Further, we have shown that sulphamineparatoluic acid is converted by oxidation with potassium permanganate into a tribasic acid very similar to sulphoisophthalic acid. This, in all probability, is sulphoterephthalic acid, as it is tribasic and contains no nitrogen. It can be obtained in any desired quantity and will be subjected to careful study.*

III.—ON THE OXIDATION OF BROMPARAETHYLTOLUENE.

By Ira Remsen and H. N. Morse.

If the hypothesis in regard to the protective influence exerted by negative groups upon hydrocarbon residues in the ortho-position were firmly established, it is plain that it might

* Dr. L. B. Hall is engaged in the thorough investigation of the compounds here mentioned as derived from paraxylene. Instead of starting from paraxylene, however, he makes use of cymene, and obtains the same products.

be made use of for the purpose of determining the structure of some compounds at present not understood. Suppose, for example, we introduce into any aromatic hydrocarbon containing two residues some negative group, and then subject the product to the action of potassium pyrochromate and sulphuric acid. *If a stable monobasic acid is produced*, then the negative group occupies the ortho-position with reference to the residue which remains unchanged. While it would be premature to state that the hypothesis upon which this method of proof is based is firmly established, it seems extremely probable that the statement may soon be made with confidence. In the meantime we have performed the experiments to be described in this article, leaving for further investigations to decide whether the arguments employed are valid or not. Whatever may be the ultimate fate of the hypothesis, however, the facts embodied in this description will of course remain facts, though the interpretation of them may be found to be incorrect.

Within the past few years a great many experiments have been performed with the object of determining the influence which one substituting group exerts upon a second or third entering the same benzene-nucleus. These experiments have been confined to cases in which the most common substituting groups or atoms, as Cl, Br, NO_2, SO_3H, etc., were studied with reference to their influence upon one another, or with reference to the influence exerted upon them by such groups as hydrocarbon residues, or by CO_2H, CH_2OH, NH_2, etc. Interesting generalizations have been reached. It is now known that all the so-called negative groups are influenced in essentially the same way by hydrocarbon residues, by carboxyl, etc. But while it has been recognized that the influence of all hydrocarbon residues is the *same in kind*, the question whether there is any recognizable *difference in degree* between the influence exerted by the group CH_3, and that exerted by C_2H_5, C_3H_7, etc., has never, we believe, been the subject of definite experimental inquiry.

There are, indeed, experiments on record which bear directly upon the question, but their connection with the question has not been pointed out; and it is fair to presume that it has not been recognized. We have hence undertaken the study of the subject here suggested.

Two methods of investigation might, theoretically at least, lead to the desired results. In the first place, substituting agents might be allowed to act upon analogous compounds, one of which contains the group CH_3, the other C_2H_5. Thus, for instance, the action of bromine, sulphuric acid, etc., upon toluene, $C_6H_5.CH_3$, might be compared with their action upon ethylbenzene, $C_6H_5.C_2H_5$. It is probable that in the latter case, as in the former, we would obtain mainly derivatives belonging to the para-series, together with smaller quantities of the isomeric ortho-products; but the proportions between the two isomeric products might be different in the two cases. To take a particular case, the definite question to be answered would be: Is the relation between the quantities of the para- and the ortho-derivatives the same when bromine acts upon ethylbenzene as when it acts upon toluene?

The difficulty which first presents itself in connection with this method of investigation consists in the fact, that the relation between the quantities of para- and ortho-derivatives formed from toluene itself and any given substituting agent is by no means constant, but dependent upon circumstances. Not only so, but the circumstances which determine the relation in any case are for the most part unknown to us, and are hence not under our control. Results obtained in the manner indicated could not then at present be reliable.

In the second place, some compound might be taken in which two different hydrocarbon residues are present, and the products derived from it compared with those obtained from an analogous substance which contains only one kind of hydrocarbon residue. Thus, as a convenient example for study, we may take the ethyltoluene of the para-series. The analogous compound, paraxylene, is well known, and the action of substituting agents upon it has been the subject of careful study. All known facts justify the assumption that only one mono-substitution product can be obtained from paraxylene with any one substituting agent. It is very likely that in a compound with a symmetrical structure, as that of paraxylene is supposed to be, the substitution takes place in connection with any one of the hydrogen atoms. Which atom is actually replaced at any given instant depends merely upon which part of the molecule is first presented to the agent. In

ethyltoluene, however, there are two kinds of replaceable hydrogen-atoms, and the action of a substituting agent upon this compound may give rise to three different results, according to the way in which the groups C_2H_5 and CH_3 act upon the entering atom or group. These possible results are:

1st. The formation of a product in which the substituting group occupies the ortho-position with reference to the CH_3, and the meta-position with reference to the C_2H_5.

2d. The formation of an isomeric product, in which the substituting group occupies the ortho-position with reference to the C_2H_5, and the meta-position with reference to the CH_3.

3d. The formation of both isomeric products in various proportions.

If the two hydrocarbon residues act with the same, or nearly the same, intensity upon the entering group, it seems clear that the third result ought to follow, *i. e.* both possible isomeric products should be formed in equal or nearly equal quantities, while the formation of only one product would indicate pretty positively that one of the groups CH_3 or C_2H_5 acts more strongly than the other. According to our experiments the result actually obtained is the first of the three mentioned. The product formed by allowing bromine to act upon ethyltoluene is, we believe, that in which bromine stands in the ortho-relation to the methyl, and the meta-relation to the ethyl.

Ethyltoluene was made according to the usual method, by treating a mixture of ethyl iodide and parabromtoluene in anhydrous ether with sodium. The parabromtoluene was a perfectly pure substance which boiled at a constant temperature, and crystallized on cooling so as to form a thoroughly solid mass. The action was moderated by cooling with ice water. An evolution of gas continued for more than twenty-four hours. When the reaction was finished the mass was distilled and the collected oil subjected to fractional distillation. It consisted of considerable benzene, toluene and ditolyl, together with the desired ethyltoluene which boiled at 158°–160°. The reaction was quite unsatisfactory and the yield small, although great care was taken to insure absolute purity of the materials employed.

Those portions of the distillate which boiled between 155°

and 165° were treated in a small flask surrounded by cold water, with somewhat less than the theoretical quantity of bromine. When the reaction, which was rapid though not violent, was finished, the product was heated to drive off hydrobromic acid and the excess of bromine, and then distilled until decomposition began.

The bromine product thus obtained was treated with the usual oxidizing mixture of potassium pyrochromate, sulphuric acid and water. The mixture was gently heated for about twenty-four hours. At the end of this time the bromine product had disappeared, while the oxidation-product was present in the form of irregular lumps upon the bottom of the flask. These lumps were filtered off, washed with water, boiled with dilute sodium carbonate, the solution filtered and the acid precipitated by means of hydrochloric acid.

After filtering and washing the acid, it was converted into the barium salt by boiling it in water with pure barium carbonate. The solution of the barium salt was boiled with animal charcoal to remove a slight yellow color. After recrystallizing the salt a few times, it presented all the properties mentioned by Jannasch and Dieckmann* as characterizing the barium salt of bromparatoluic acid.

It was analyzed with the following results:

I. 0.1518 grams salt lost 0.0169 grams H_2O at 110°.

II. 0.1846 grams salt gave 0.06617 grams $BaSO_4$.

III. 0.1001 grams salt lost 0.0114 grams H_2O at 180°, and gave 0.036 grams $BaSO_4$.

	Calculated.		Found.		
			I.	II.	III.
$(C_8H_6BrO_2)_2$ ...	428	67.20	...	...	...
Ba ...	137	21.50	...	21.10	21.10
$4H_2O$ ...	72	11.30	11.10	...	11.37
	637	100.00			

The formula of the salt is thus seen to be $(C_6H_3Br.CH_3.CO_2)_2$ Ba + 4 H_2O, and this is also the formula of the known barium salt of bromparatoluic acid.

*Ann. der Chemie, 171, 84.

The calcium salt of the acid was made by boiling some of the acid recovered from the purified barium salt with pure calcium carbonate. It is only necessary to say that the salt proved to be in every respect identical with that described in the paper by Jannasch and Dieckmann referred to above. Its analysis yielded the following results:

0.2597 grams salt lost 0.0277 grams H_2O at 180°, and gave 0.0668 grams $CaSO_4$.

		Calculated.		Found.
$(C_8H_6BrO_2)_2$	...	428	81.67	...
Ca	...	40	7.66	7.55
$3H_2O$	...	54	10.67	10.37
		522	100.00	

Further, the free acid possessed all the properties attributed to it by those who have previously described it. Its melting point was found to be 203°–204°.

Finally, the acid was treated with sodium amalgam for some hours. The bromine was thus extracted, and an acid obtained which exhibited all the properties of paratoluic acid. It crystallized from water, and fused at 178°.

It can not be doubted, then, that the bromine product formed by treating ethyltoluene with bromine yields bromparatoluic acid when subjected to the action of chromic acid. The mother-liquors from the first crystallizations of the barium salt were carefully examined, and no evidence was obtained of the presence of a second salt. The oxidizing mixtures were also examined, and nothing but a very small quantity of an acid was found which differed at all from bromparatoluic acid. The quantity of the acid was so small that we were unable to examine it thoroughly. It was found to fuse between 195° and 200°. The barium salt and the acid itself did not differ enough from bromparatoluic acid and its barium salt to make it appear at all improbable that the acid was simply impure bromparatoluic acid.

The interpretation of the transformations here described we believe to be a simple matter. We believe that the methyl group is protected from oxidation because it stands in the ortho-relation to the bromine atom, while the ethyl is oxidized because it stands in the meta-

relation to the bromine. Or, adopting
the usual method of representation, the
formula of brom- ethyltoluene is, accord-
ing to these ideas, Of course, this conclusion
can, at present, be only regarded as pre-
liminary, for, until the results of more
experiments have been described, the hypothesis upon which the proof for this formula is dependent can hardly be considered as established. Assuming the formula to be correct, however, what does it indicate?

We know that when a negative group enters toluene its tendency is to take mainly the para-position. The influence of the hydrocarbon residues is, as is said, to repel the negative group. But, plainly, until we know that the para-position is really further removed than the ortho-position, this statement can only be figurative and directly dependent upon the scheme of Kekulé for its meaning. It is true that the peculiar cases of condensation noticed in connection with ortho-compounds, among which may be mentioned the formation of phthalic anhydride, of salicylic anhydride, etc., etc., do really seem to show that groups in the ortho-position with reference to each other are more closely connected than groups in the other positions; but there are not enough facts known as yet to warrant the expression of a decided opinion upon this subject.

The formation of the bromethyltoluene represented by the formula given shows that one of the groups acts more strongly upon the bromine atom than the other, for, as remarked above, if both groups acted with equal intensity, two isomeric products should have been obtained. While we can not tell which group acts with the greater intensity by examining the formula, the following reasoning seems to be justifiable. If, as is commonly stated, CH_3 repels negative groups, then we would expect C_2H_5 to exert the same kind of action more strongly, as any force exerted by either group must be dependent to some extent upon the mass of the group, and the mass of C_2H_5 is greater than that of CH_3. Assuming this to be the case, and assuming, further, that the para-position is further removed than the ortho-position, then it would follow that the meta-position is also further removed than the ortho-position, otherwise the bromine ought to take the ortho-posi-

tion with reference to that group which exerts the stronger action.

Although these latter considerations can lead us at present to no positive conclusions, still they are interesting as indicating a possible future method of investigation. The proofs for the structure of bromparatoluic acid are, however, independent of the the theory in regard to the nature of benzene.

One objection may be made to the proof. It may be said that even though the conclusion with reference to the protective influence exerted by the bromine upon the group situated in the ortho-position be acknowledged, it would still be possible to obtain bromparatoluic acid from a body of the structure

For the CH_3 might be converted into carboxyl, and the C_2H_5 group be broken up by the oxidizing mixture, so as to leave CH_3 in its place. This does not appear probable in the light of all known facts, but still we could easily decide this point by oxidizing bromparadiethylbenzene. If the C_2H_5 group can break up in the manner indicated, then the product would be bromparatoluic acid; whereas, if it does not break up, the product will be bromparaethylbenzoic acid.

Among experiments which have been performed by others and which bear upon the question discussed in this paper, may be mentioned those which have proved that, by oxidation of monosubstitution products of cymene (parapropyltoluene), derivatives of paratoluic acid are obtained. Thus Landolph has shown* that monobromcymene yields monobromparatoluic acid. Fittica† has performed the same experiment with the same result. Fittica‡ has also shown that cymene, when treated with concentrated nitric acid, yields nitroparatoluic acid, which is identical with that obtained by the oxidation of nitroparaxylene, and by treatment of paratoluic acid with nitric acid. It must be stated in this connection, however, that both Landolph and Fittica obtained two mononitro-derivatives from cymene, and, according to Fittica, each of these derivatives yields a different nitro-acid when oxidized. If two nitro-acids can be obtained in this way, it seems possible that one of them may prove to be not nitrotoluic but

* Ber. d. chem. Gesell., 5, 267. †Ann. der Chemie, 172, 303. ‡Loc. cit.

nitroparapropylbenzoic acid. Indeed, according to a recent notice* by v. Gerichten, the substance formerly described by Landolph and by Fittica as solid nitrocymene has not the composition of nitrocymene at all, hence it may well be doubted whether the product described as a new nitrotoluic acid has the composition ascribed to it. Again Flesch† succeeded in forming sulphotoluic acid by oxidizing thiocymene. Bechler‡ also obtained a sulphotoluic acid in the same way, while Fittica§ states that the sulphotoluic acid which is produced by oxidizing thiothymocymene with nitric acid is not identical with that described by Flesch and by Bechler.

To the cases of the chlorcymenes and bromcymenes studied by v. Gerichten reference was made in the preceding article. We may, however, here call attention to the interesting fact that after v. Gerichten's first publication in which he claimed to have prepared two isomeric chlortoluic acids from the two isomeric chlorcymenes, we publicly‖ expressed doubt in regard to the accuracy of his work, and suggested that one of the chlortoluic acids might prove to be chlorparapropylbenzoic acid. Shortly afterward v. Gerichten published a notice in which he acknowledged that one of his acids had actually the composition of a chlorpropylbenzoic acid as we suggested. Later, however, he believes that he has proved this acid to be ethylchlorhydrocinnamic acid. The uncertainty connected with his last conclusion, however, is so great, as was pointed out in the previous article, that for the present we feel justified in waiting for further proofs of its correctness. We feel this way, particularly as there are now so many cases known which show that the views held by us in regard to the conduct of aromatic substitution products under the influence of oxidizing agents are correct, and there is really only this last one uncertain case which in any way speaks against our views.

* Ber. d. chem. Gesell., 11 1091. † Ib., 6, 481. ‡ Journ. prak. Chemie, 116, 167.
§ Ann. der Chemie, 172, 328. ‖ Ber. d. chem. Gesell., 11, 282.

NOTE ON THE DETERMINATION OF SILICON IN PIG IRON AND STEEL.*

By Thomas M. Drown.

In experimenting in connection with Mr. P. W. Shimer (now chemist of the Thomas Iron Company, Hokendauqua, Pa.) on methods for the determination of silicon in pig iron, in order to find one which should be accurate and yet give results in a few hours, I have adopted the following procedure, which, as far as my experience goes, leaves nothing to be desired.

About one gram of pig iron or steel is treated in a platinum or porcelain dish with 25 cubic centimeters of nitric acid (sp. gr. 1, 2). When action has ceased, 25 to 30 cubic centimeters of dilute sulphuric acid (one of acid and three of water) are added, and heat applied until the nitric acid is nearly or quite driven off. The heat of a water-bath is sufficient, though the process may be hastened by heating higher on a sand-bath. Water is then cautiously added (as soon as the free sulphuric acid is sufficiently cool) and the contents of the dish heated until the crystals of ferric sulphate are completely dissolved. The solution is then filtered *as hot* as possible, the residue washed first with hot water, then with 25 to 30 cubic centimeters of hydrochloric acid (sp. gr. 1, 12), and finally with hot water. After drying and igniting, the silica will be found to be snow-white and granular.

The following are some results obtained by this method compared, in some instances, with the older method of treatment with nitric acid, evaporation to dryness, heating to 150° C. for several hours, dissolving out the iron in hydrochloric acid, and filtering off from the insoluble residue, which is dried and ignited, and the resulting impure silica fused with alkaline carbonates.

The letters denote different samples of pig iron.

* Read before the American Institute of Mining Engineers. Communicated by the Author.

	Per Cent. of Silicon.							
	A	B	C	D	E	F	G	Bessemer steel.
Old method.....	2.64	2.46	.....	1.45	1.65	.....	.....	.672
New method, 1...	2.70	2.47	1.13	1.63	1.53†	1.66	2.50	.676
" " 2...	2.68	2.47	1.18	1.62	1.51†	1.68	2.50	.672
" " 3...	2.81*	2.47	.....	1.65	1.51†	1.72	2.50	.672
" " 4...	.....	.....	.....	.....	1.63‡	1.70	2.47	.....
" " 5...	.....	.....	.....	.....	1.65‡	.....	2.46	.....
" " 6...	.....	.....	.....	.....	1.65‡	.....	.....	.....

*Not washed with hydrochloric acid.

†In these analyses hydrochloric acid was used after the addition of nitric acid, and was not completely driven off.

‡Hydrochloric acid was used for solution instead of nitric acid.

Some incidental results obtained in developing this process have enough interest to be worthy of record. Treatment of pig iron with concentrated sulphuric acid, heating till fumes arise, diluting with water, and filtering after all action has ceased, gives a silica which is seldom pure, and yet the results are considerably too low.

Treatment with dilute sulphuric acid and evaporation till the acid fumes in the air, then filtering after dilution, gives occasionally results which are accurate; but this method is uncertain, depending on the fineness of the borings and character and composition of the pig iron. The silica obtained is seldom white. The following are some results obtained in this way:

	Per Cent. of Silicon.			
	A	B	C	D
Old method	1.02	1.64	2.64	3.85
New method, 1.....	1.05	1.73	3.00	3.88
" " 2.....	1.05	1.69	2.98	3.91
" " 3.....	1.05	1.70	2.97	.....
" " 4.....	.....	.....	3.01	.....

Treatment in platinum dishes gave very slightly lower results than porcelain dishes.

If after treatment with dilute sulphuric acid the solution is filtered off from the residue without concentration of the acid, it is found that about one-half of the silicon is in the solution and the other half in the residue; when nitric acid is used and the solution filtered off as soon as all action has ceased, it is found that about two-thirds of the silicon is in the solution and one-third in the residue; and with hydrochloric acid, about one-third goes into the solution and two-thirds remains in the residue. It is not probable that there is any precise ratio existing between the amount of silicon dissolved and the amount in the residue in the case of any one of the acids, the ratio being doubtless variable and depending on the concentration of the acid, the time of action, and the temperature; yet the marked difference in the action of the three acids in this respect is interesting.

The washing with hydrochloric acid of the residue obtained by the action of nitric and sulphuric acids on pig iron is in most cases necessary. Thus there was obtained from the pig iron when water only was used for washing, 2.67 per cent. of silicon against 2.52 when washed with hydrochloric acid; and in another sample, 2.10 per cent. against 1.70 per cent.

Although the results obtained with hydrochloric acid for the original solution of the iron show, as far as the experiments go, as good results as those obtained with nitric acid, yet I prefer the nitric acid treatment on account of the silica obtained being compact and granular, while the use of hydrochloric acid, and also of sulphuric acid alone, yields a silica which is light and flaky.

EASTON, PA., *February*, 1879.

ON A NEW BASE.

By Edgar F. Smith.

In the *Proceedings of the Am. Phil. Soc.* for May 4, 1877, and *Jahresbericht*, 1877, Heft i. p. 420, may be found a paper containing a description of several new chlorine derivatives of toluene. One of these, to which especial interest attaches itself, is a *carbon chloride* having the following empirical formula $C_{21}Cl_{26}$. It was obtained by treating toluene with dry chlorine until the gas was no longer absorbed. The new derivative when pure formed large colorless prisms which fused at 152°–153°C. It possessed an odor very much like that of camphor. In water and alcohol it was insoluble, while chloroform dissolved it readily.

Action of Aniline upon $C_{21}Cl_{26}$.

A quantity of the above compound, finely divided, was heated in a sealed tube with an excess of aniline for six or eight hours. The temperature during this time did not exceed 180°C. Upon examination after cooling a deep red colored, viscid product was discovered, which was transferred to a shallow dish, water added, and the whole then heated upon a water-bath. In this manner much of the adherent aniline was expelled. By repeatedly distilling the residue remaining after evaporation it was finally obtained pure.

Properties.—The new base produced in the above manner contains chlorine and nitrogen. It forms salts with acids. In water, and indeed all solvents, it is exceedingly easily soluble. From the most concentrated aqueous solutions it is obtained only after long standing, when it separates in thin broad scales, which carbonize slightly at 225°C, and fuse at 230°C. The crystals are almost colorless; they refract light strongly.

Upon gently heating a portion of the base with an aqueous solution of chromic acid, a reddish brown flocculent mass was precipitated. This was filtered and washed. In hot water it dissolved sparingly; more soluble in alcohol, to which it im-

parted an intense red color. On the addition of zinc and dilute hydrochloric acid to the highly colored solution, the latter was slowly decolorized, but upon warming the liquid the color again appeared.

Hydrochloric Acid Salt.—Upon evaporating a portion of the above base with hydrochloric acid and repeatedly recrystallizing the residue, the salt was procured in very long, broad, colorless crystals.

In water and alcohol the salt is readily soluble.

Analysis.—.1115 grams dried salt dissolved in water and treated with silver nitrate gave .1283 grams AgCl, yielding .0317 grams Cl, corresponding to 28.43 per cent. chlorine.

The investigation of the various derivatives of $C_{21}Cl_{26}$ advances slowly owing to the fact that this compound is obtained with great difficulty; the cold of winter is necessary for its formation.

LABORATORY OF THE UNIVERSITY OF PENNA., *April* 17, 1879.

LABORATORY NOTES FROM THE UNIVERSITY OF CINCINNATI.*

X.—ON SOME NEW SALTS OF ANILINE.

BY MILES BEAMER AND F. W. CLARKE.

The following salts of aniline, which seem to have been hitherto undescribed, we have lately prepared and partially examined.

Aniline Chlorate.—This salt is formed by the direct union of aniline and chloric acid. When aniline is added to a dilute aqueous solution of the acid, white crystals almost immediately appear. These, however, if exposed to the air while damp, are rapidly decomposed, and in the course of a few moments become

* The earlier numbers of this series of notes appeared in the *American Journal of Science and Arts*, for April and October 1877, and September 1878.

black. A better way to prepare this very unstable body is to cautiously add chloric acid to an alcoholic solution of aniline, and then to evaporate under the receiver of an air-pump. By operating thus upon a small quantity of material in a watch-glass, long, white, slender prisms of over an inch in length were obtained.

Aniline chlorate is very readily soluble in alcohol and ether, but less soluble in water. On exposure to air, or upon even gentle heating, its solutions blacken and decompose. The thoroughly dried substance, however, may be preserved for a day or more without change. It detonates sharply when struck; and in common with other chlorates it decomposes explosively when brought in contact with concentrated sulphuric acid. When heated to 75°–76° it also explodes. This temperature was fixed by repeatedly heating crystals of the salt upon the surface of mercury into which a thermometer dipped. Heat was cautiously applied to the mercury, and the exploding point was thus ascertained with considerable accuracy.

Aniline Perchlorate.—The preparation of this compound was similar to that of the chlorate. Dilute perchloric acid was added to an alcoholic solution of aniline, and the mixture was evaporated *in vacuo*. The crystals are tolerably large rhombic plates, not nearly so unstable as those of the chlorate, and when dry are permanent in the air. They detonate feebly when struck or heated, and are decomposed by sulphuric acid. The exact temperature of decomposition could not be ascertained.

Aniline Iodate.—When aniline is added to a solution of iodic acid, this body is copiously precipitated in the form of white scales, which may be dried between folds of filter-paper. It is very slightly soluble in cold water, more soluble in hot water, and more so still in boiling alcohol. From the latter solvent it is deposited on cooling in beautiful nacreous scales. All of its solutions slowly decompose upon standing, and even the dry substance becomes discolored by long exposure to the air. When heated slowly to 110° it blackens; but no further change takes place, even when the temperature is carried as high as 150°. By sudden heating, however, it explodes at 125°–130°. On percussion it detonates very feebly, yielding a

dense cloud of smoke which is light brown by reflected, and violet by transmitted light. When thrown upon sulphuric acid it instantaneously decomposes in a similar way, yielding the same dense vapors. Specific gravity 1.48 at 13°.

Aniline Fluohydrate.—Beautiful pearly scales formed by the union of aniline and fluohydric acid. It is very soluble in boiling alcohol, but separates out from the solution so rapidly upon cooling as to completely choke up the throat of the funnel through which it is filtered.

Aniline Phthalate.—Formed by the addition of aniline to an alcoholic solution of phthalic acid. The salt crystallizes very readily in clusters of concentric needles. Melting-point 145°–146°.

Aniline Monochloracetate.—Upon adding aniline to a solution of monochloracetic acid this salt is soon deposited in a flocculent mass of white crystals. These, when dissolved in warm (not hot) water, and recrystallized *in vacuo*, reappear as long, white, slender needles, of melting-point 88°. By boiling the aqueous solution of the compound it is decomposed.

Aniline Dichloracetate.—Formed like the monochloracetate. It crystallizes in long white prisms, which melt at 122°.

Aniline Trichloracetate.—Prepared by dissolving aniline in an aqueous solution of trichloracetic acid. From dilute solutions it is deposited in crystalline plates, piled step-wise one upon another. When crystallized more rapidly, that is, from a more concentrated solution, it appears as large, thin, transparent rhombic plates, somewhat resembling mica. Either form of crystals heated to 50° becomes white and opaque, but undergoes no loss of weight. This opaque modification, recrystallized, is reconverted into the original transparent variety. Melting-point 145°.

Of these salts, the iodate and trichloracetate are being farther investigated.

XI.—NOTE ON LITHIUM PICRATE.

By Miles Beamer and F. W. Clarke.

Lithium carbonate dissolves readily in an alcoholic solution of picric acid; and, on spontaneous evaporation, long, slender prisms of anhydrous lithium picrate are obtained. Like other

picrates the salt is bright yellow, and detonates feebly upon percussion. When heated to 200° it blackens, but no further change ensues even when the temperature is carried to 260°. Heated suddenly in a flame, however, it explodes with great violence. Specific gravity 1.716 at 19° ; 1.724 to 1.740 at 20°.

XII.—PRELIMINARY NOTICE OF A NEW VOLATILE ALKALOID.

By W. L. Dudley.

Spigelia marilandica, or pink-root, has been known for many years to possess peculiar medicinal properties, seemingly indicative of the presence of an alkaloid. According to the published analysis of the root by M. Fenuelle, however, it contains "a fixed and volatile oil, a small quantity of resin, a bitter substance, a mucilaginous, saccharine matter, albumen, gallic acid, the malates of potash and lime, &c., and woody fibre."

Since the activity of *spigelia* is somewhat diminished by time, I suspected the presence of a volatile alkaloid, and began a search for the same. About two kilograms of the dried root were ground, inserted in a flask, mixed thoroughly with milk of lime, and distilled over a paraffin bath. The distillate was collected in a receiver containing hydrochloric acid, and evaporated to dryness over a water-bath. The residue was then extracted with absolute alcohol, the solution filtered and allowed to evaporate spontaneously to dryness. A small amount of crystalline substance remained, which was soluble in water, and which gave the following reactions, differing from those of the previously known volatile alkaloids. In the accompanying table these reactions are compared with some of those given by nicotina, conia, and lobelina :—

	Spigelina.	*Nicotina.*	*Conia.*	*Lobelina.*
Iodine in a KI solution.	Brownish red precipitate.	Brownish red precipitate.	Pale brownish red precipitate.	Brownish red precipitate.
Potassio-mercuric iodide.	White crystalline precipit.	Yellowish precipitate.	Like nicotina.	Pale yellow precipitate.
Metatungstic acid	White flocculent precipit.			

The precipitate formed by potassio-mercuric iodide with spigelina is soluble in acids, in alcohol, and in ether, but insoluble in an excess of the precipitant. In these points it differs clearly from the precipitates given by the other volatile alkaloids.

An insufficient supply of material rendered farther investigation at the time impossible; but enough was done to distinctly indicate the presence of a new volatile base, to which I naturally apply the name of spigelina.

ON HEPTANE FROM PINUS SABINIANA.*

By T. E. Thorpe, Ph. D., F. R. S.,
Professor of Chemistry in the Yorkshire College, Leeds.

In a paper read to the California Pharmaceutical Society on December 13, 1871, and reprinted in the *Pharmaceutical Journal* for March 30, 1872, Mr. William Wenzell, of San Francisco, describes as new and under the name of *Abietene*† a hydrocarbon obtained by distilling the terebinthinate exudation of a coniferous tree, *Pinus sabiniana, Dougl.* This tree is indigenous to California, and grows on the dry slopes of the foothills of the Sierra Nevada, and on the hills along the coast; it appears to be pretty plentiful, and is known locally as the nut pine or Digger pine, names suggested by the circumstance that the Digger Indians rely to some extent on its fruit for food.

In order to procure the exudation, the tree during winter is notched and guttered at a convenient height from the ground, and the resin on distillation yields the liquid hydrocarbon. The crude oil is met with in San Francisco as an article of

* Communicated by the Author.

† The name *Abietin* was applied by Caillot to a resin obtained from the turpentine of *Abies picea* and *Abies balsamea.*

commerce, and during the last few years has acquired some reputation under the names of "abietene," "erasine," "aurantine," "theoline," &c., as a substitute for "benzoline" or "petroleum benzene" for removing grease-spots, paint-stains, &c., from clothing. It is a nearly colorless mobile liquid of powerful aromatic smell, recalling that of oil of oranges. The crude oil, according to Mr. Wenzell, boils almost entirely between 100° and 105°, and on redistillation the liquid is obtained of the constant boiling-point of 101°. The portion boiling above 105° leaves on evaporation a small quantity of a resinoid body, possessing the strong penetrating odor of the original product. The liquid is highly inflammable and burns with a brilliant white smokeless flame. Its vapor is powerfully anæsthetic, and it has been used with success as an insecticide.

No analysis or vapor-density determination of this liquid is given in the communication above referred to, nor does Mr. Wenzell offer any opinion as to its real nature. He contrasts its characters with those of terebene (spirits of turpentine), the hydrocarbon obtained from *Pinus palustris*, *P. sylvestris*, &c., and points out the very striking differences observed in their physical and chemical properties. Abietene has a sp. gr. of 0.694 at 16.5°, whilst that of terebene is 0.840 at about the same temperature. Oil of turpentine boils at 160°, whilst the boiling-point of abietene is 101°. Hydrochloric acid gas is but slightly dissolved by abietene, whereas oil of turpentine absorbs it with avidity. Nitric acid acts violently on oil of turpentine; it has little or no action on abietene in the cold.

Abietene was evidently sufficiently remarkable to merit further investigation. From its general behavior towards reagents it seemed not unlikely that it would prove to be a paraffin, and the boiling point and sp. gr. appeared to indicate *normal heptane*. The occurrence of heptane, or indeed of any other paraffin, playing the part of oil of turpentine in the vegetable kingdom was hitherto unheard of. The only natural source of this hydrocarbon was petroleum or some of the fossil-fish oils obtained in Greenland, Switzerland, and other places. Menhaden oil contains considerable quantities of heptane, and it is met with among the products of the destructive distillation of cannel and shale.

Through the kindness of Mr. H. B. Brady, F. R. S., I was able to obtain, through Dr. Squibb, of New York, about a couple of gallons of abietene from Mr. Wenzell. The crude oil fully answered the description already given of it by the latter gentleman. It was almost colorless, and had the strong persistent odor of oil of oranges. It began to boil slightly below 100°, and the greater part distilled below 101°. The residual portion darkened slightly, and on evaporation left a small quantity of resinoid matter of a brown color which had the peculiar smell of the liquid in a very high degree. This led to the supposition that the odor of the crude oil might be due in great part to the resin in solution, and further examination proved this to be the case. On agitating it for some time with oil of vitriol, the acid became brown, and on again distilling the hydrocarbon was found to have lost its smell of orange oil.

Two determinations of its boiling-point were made by the aid of a thermometer capable of being read to 0.01°C. The first observation gave 98.27° at 755.6 mm., the second 97.93° at 746.9 mm. The mercurial columns in both cases were wholly immersed in the vapor, and the barometric pressures are corrected and reduced to 0°C. Assuming the validity of the well-known expression—

$$T = t + 0.0375(b - 760),$$

where t is the observed boiling point and b the barometric pressure, the boiling point, T, under the standard pressure becomes respectively—

I. . . . 98.43°
II. . . . 98.42

The first determination was made on about three litres of the liquid, the second on about 250 cc., after a second treatment with a mixture of nitric and sulphuric acids; in both cases the liquid boiled as constantly as distilled water. In all I obtained about seven litres of the perfectly pure substance from seven and a half litres of the crude oil.

That abietene is actually heptane is proved by the following analyses and determinations of vapor-density:

I. 0.3500 gram hydrocarbon gave 1.0754 gram CO_2 and 0.5050 gram O_2H.

II. 0.3000 gram hydrocarbon gave 0.9215 gram CO_2 and 0.4336 H_2O.

	Calculated for C_7H_{16}.	Found. I.	Found. II.
C ...	83.97	83.85	83.78
H ...	16.03	16.03	16.06
	100.00	99.88	99.84

Two determinations of its vapor-density, made in a modified form of Hofmann's apparatus,* gave the following results:

I.	Weight of liquid	144.5 mgm.
	Volume of vapor (corrected for expansion of glass, error of meniscus, &c)..	90.39 cc.
	Temperature of vapor	99.90°C.
	Barometer (corrected and reduced)	757.6 mm.
	Height of mercury in tube (reduced)	387.8 "
II.	Weight of liquid	76.9 mgm.
	Volume of vapor (corrected)	69.77 cc.
	Temperature	99.60° C.
	Barometer	749.0 mm.
	Height of mercury in tube	493.4 "

Calculated for C_7H_{16}.	Found. I.	Found. II.
49.90	50.07	49.94

I. *The Physical Characters of Heptane from Pinus Sabiniana.*

The possession of so large a quantity of perfectly pure heptane has induced me to study some of the physical characters of this hydrocarbon. These observations have included the determination of its specific gravity, and the measurement of its thermal expansion, refractive index, optical activity, viscosity, and superficial tension.

Specific Gravity.—Three determinations of specific gravity made with different bottles gave the following results:

* The apparatus here referred to allows of the determination of a vapor-density with almost as much exactitude as that of any other physical constant; it was designed more especially with a view of controlling the purity of some liquids employed in a research involving the determination of a number of thermal expansions.

0.68848 at 14.98°
0.68855 " 14.87
0.68858 " 14.87

compared with water at the same temperatures respectively. The weighings were made by the method of vibrations and the weights are reduced to a vacuum. Reducing these results by the aid of Rossetti's tables for the expansion of water, and by means of the formula for the thermal expansion of heptane given below, the specific gravity at 0°, compared with water at 0°, becomes respectively—

0.70057
0.70055
0.70058

Mean... 0.70057

Thermal Expansion.—The rate of expansion of the heptane was determined by heating the hydrocarbon in dilatometers properly calibrated and graduated. The volume of the hydrocarbon at 0° was obtained by immersing the dilatometers in melting snow. The instruments were then placed in a large copper bath fitted with plate-glass sides, and holding several litres of water, which could be kept in constant motion by stirrers worked by a small hydraulic engine. The water was heated by steam and the temperature ascertained by thermometers capable of being read to 0.01° C.

Two series of observations were made. The first set gave the following results:

Temperature.*	Observed volume.	Calculated volume.	Temperature.	Observed volume.	Calculated volume.
0.00	3290.1	3290.4	53.71	3516.3	3516.9
9.04	3326.1	3326.0	62.80	3560.1	3559.9
17.27	3359.2	3359.1	72.12	3606.2	3605.7
26.96	3398.9	3399.1	80.68	3649.5	3649.5
35.55	3435.9	3435.7	87.32	3684.2	3684.6
44.96	3477.2	3477.1	93.70	3719.9	3719.4

*These temperatures are expressed in degrees of the air thermometer in order to make them uniform with my other observations of thermal expansion. The conversion from the ordinary thermometric values is effected by a table compiled from Regnault's and Recknagel's comparisons of the air and mercurial thermometers (see Wuellner's *Lehrbuch der Physik*). To convert the degrees of the air thermometer into those of the mercurial thermometer *add* 0.08° at 10°, 0.16° at 25°, 0.16° at 65°, 0.1° at 80°.

Combining the results by the method of equation of conditions, we obtain the formula—

$$3290.361 + 3.895352\,t + 0.00432087\,t^2 + 0.00003183\,t^3,$$

by means of which the numbers in the third column of the above table are calculated.

The second series, made in a different dilatometer, gave the following data:

Temperature.	Observed volume.	Calculated volume.	Temperature.	Observed volume.	Calculated volume.
0·00	2879.6	2879.3	53.71	3076.4	3077.0
9·04	2910.5	2910.6	62.81	3114.5	3114.5
17.27	2939.3	2939.5	72.13	3155.2	3154.7
26.97	2974.2	2974.5	80.68	3193.6	3193.2
35.54	2006.4	3006.2	87.27	3223.8	3224.1
44.96	2042.3	3042.3	93.71	3255.3	3255.4

These numbers afford the expression—

$$2879.302 + 3.432882\,t + 0.00247831\,t^2 + 0.00003964\,t^3,$$

by the aid of which the numbers in the third column of the above table are computed.

Dividing through by the first terms respectively, and correcting for the expansion of the glass of the dilatometers (0.00002130 for 1° in Series I, and 0.00002303 in Series II), the formulæ become—

I. $1 + 0.00120517\,t + 0.00000133841\,t^2 + 0.000000009701\,t^3,$

and

II. $1 + 0.00121529\,t + 0.00000088819\,t^2 + 0.000000013787\,t^3.$

The mean formula is—

$$1 + 0.00121023\,t + 0.0000011133\,t^2 + 0.00000001174\,t^3,$$

by the aid of which the following table, showing the relative volumes of heptane from *Pinus sabiniana* at every 5° between 0° and 100° is calculated—

Temperature.	Volume.	Difference.	Temperature.	Volume.	Difference.
0	100000	—	55	107188	712
5	100608	608	60	107916	728
10	101222	614	65	108659	743
15	101844	622	70	109420	761
20	102474	630	75	110198	778
25	103114	640	80	110995	797
30	103763	649	85	111812	817
35	104423	660	90	112650	838
40	105094	671	95	113509	859
45	105778	684	100	114390	881
50	106476	698			

The volume at the boiling point 98.43 is 1.14111; hence the specific gravity at this temperature is 0.61393, which gives for heptane *the specific volume* 162.54. Kopp's values (C = 11; H = 5.5) afford the number 165.

Refractive Index.—A careful set of observations of the index of refraction of heptane from *Pinus sabiniana* was made for me by Mr. John I. Watts in the Physical Laboratory of the Owens College, Manchester, by one of Elliott's horizontal goniometers.

Five concordant determinations of the angle of the prism employed gave as a mean result:

$$\theta = 59° \ 12' \ 20''.$$

The same number of observations of the angle of minimum deviation gave:

$$\delta = 27° \ 21' \ 44''.$$

The source of light was a sodium flame. The temperature of the liquid was 17.6°.

Inserting these numbers in the the well-known formula

$$\mu = \frac{\sin. \frac{1}{2} (\delta + \theta)}{\sin. \frac{1}{2} \theta},$$

we obtain 1.3879 as the refractive index for D.

The *specific refractive energy*, $\frac{\mu - 1}{d}$, where d is the specific gravity of the liquid at 17.6° is 0.565; whence the *molecular*

refractive energy is 56.4 in close accordance with the computed number 55.8, calculated by Landolt's values, C = 5, H = 1.3.

Optical Activity.—It is well known that the various terpenes are optically active, often to a very remarkable extent; hence a special interest seemed to be attached to the question of the behavior of the heptane of *P. sabiniana* towards polarized light. Through the kindness of Prof. Gamgee, Mr. J. H. Poynting was able to make a number of observations on the hydrocarbon by means of an excellent Laurent's polarimeter belonging to the Physiological Laboratory of the Owens College. These observations seem to indicate that the heptane does actually rotate the plane of the polarized ray, although to a very slight extent only, a column 200 mm. long exhibiting a rotatory power of +6.9′. This amount is so small that I was disposed to attribute it to the possible presence of impurities, despite the careful rectification to which the hydrocarbon had been subjected: the original exudation might have contained small quantities of a terpene, or a minute trace of the resinous matter which it has been stated the crude oil leaves on evaporation might still be contained in the distilled hydrocarbon. The liquid with which Mr. Poynting experimented was accordingly agitated with a mixture of concentrated nitric and sulphuric acids at frequent intervals for several days, but the acids remained perfectly colorless, and the hydrocarbon after redistillation showed precisely the same rotatory power as before, viz., + 6.9′. I am inclined to believe, however, that an optically active terpene is actually present in crude abietene, although not to a greater extent than 0.5 per cent.: the liquid residue left on distilling the crude oil boiled between 140° and 160°, and showed a rotatory power of —12° 23.5′: this liquid, it should be noted, had not been treated with acids. The resin itself, in alcoholic solution, appears to be optically inactive.

Viscosity.—The capillary transpiration of the heptane from *Pinus sabiniana* was determined by a method identical in principle with that already employed by Poiseuille, Graham, and others; this consists in noting the time required for a given volume of the liquid at some particular temperature and under a uniform pressure to flow through a cylindrical capillary tube of known dimensions. The capillary tube employed was

85.4 mm. in length and 0.2105 mm. in internal diameter: it was sealed, at right angles, to a long cylindrical bulb, containing between two marks etched on the narrow tube above and below the bulb 14.7755 cc. The open end of the capillary tube was connected with a receiver, and the whole was so arranged that it could be wholly immersed in a large bath fitted with plate-glass sides and holding several gallons of water. The temperature of the bath, and therefore of the hydrocarbon contained in the bulb and tubes, could be raised to any desired point below about 80° by heating a coil of copper tube affixed to the side of the bath through which the water from the bath continually circulated. The liquid in the bath was kept in constant agitation by means of stirrers worked by a small hydraulic engine; and the temperature was ascertained by a thermometer capable of being read to 0.01°C. The hydrocarbon was drawn into the bulb by the aid of the air-pump, and as soon as it had acquired the temperature of the bath it was forced through the capillary tube by the pressure of a confined volume of air kept at a nearly constant tension of 111.2 mm. of mercury by the weight of a column of water of uniform height; and the times at which the level of the liquid passed the two marks, as observed through a telescope, were noted on a chronometer. This apparatus has been employed by Mr. John Muir, student in the Laboratory of the Yorkshire College, in the determination of the viscosity coefficients of a number of liquids; a detailed description of it is reserved for a communication containing the results of his experiments.

Two independent series of observations were made with heptane with the following results:—

Series I.

Temperature.	Time (seconds).	V.	η.	Temperature.	Time (seconds).	V.	η.
6.72°	931.7	7313	.005268	35.07°	611.1	11151	.003454
10.27	794.3	8579	.004490	40.16	582.2	11704	.003292
15.31	749.3	9094	.004236	44.75	560.4	12159	.003168
20.05	710.9	9585	.004019	49.70	534.7	12745	.003023
25.06	673.8	10113	.003810	54.84	512.0	13309	.002895
29.95	642.9	10599	.003635				

Series II.

Temperature.	Time (seconds).	V.	η.	Temperature.	Time (seconds).	V.	η.
7.09°	845.0	8064	.004777	30.06°	639.6	10654	.003616
10.31	792.9	8594	.004482	35.03	611.6	11141	.003457
15.30	749.3	9094	.004236	39.16	585.2	11645	.003300
20.15	713.0	9557	.004031	45.37	555.7	12262	.003142
25.09	673.6	10116	.003808	49 30	538.0	12666	.003042

The transpiration times are corrected for any slight irregularities in the pressure (these never exceeded 0.4 mm. of mercury), and for the change in the dimensions of the bulb and capillary tube by heat.

If Q be the volume of the liquid flowing through the tube in the time t, p the pressure under which it is driven expressed in millimeters of water, l the length of the tube, and r its radius in millimeters, then the volume, V, in cubic millimeters flowing in one second of time through a tube 1 mm. long, 1 mm. radius, and under a pressure of 1 mm. of water, on the assumption that Poiseuille's laws hold good under these conditions is given by the formula—

$$V = \frac{Q \cdot l}{t \cdot p \cdot r^4}.$$

The numbers so obtained are given in the third column of the above tables.

If all the particles of the moving liquid are flowing in parallel straight lines, with velocities proportional to their distances from a plane parallel to these lines, then of any two contiguous layers, the motion of that which moves the more rapidly will be retarded by a force (viscosity) dependent, *cæteris paribus*, on the nature of the liquid, and varying with its temperature. The coefficient of viscosity in absolute measure is the force expressed in dynes thus exerted on a liquid surface one square centimeter in area, lying in a plane of uniform velocity, when the difference of the velocities of two layers one centimeter apart is one centimeter per second.

The viscosity coefficients, η, of heptane for the particular

temperature given in the table are directly obtained from the values of V in absolute measure by the expression—

$$\eta = \frac{\pi \cdot 98.1}{8 \cdot V}$$

by means of which the numbers in the last columns of the above tables are calculated.

It will be noticed that the viscosity suddenly diminishes at some point between 8° and 10°. After the latter temperature has been reached the rate of diminution is very regular, and may be represented by an expression of the form—

$$\eta = a + bt + ct^2.$$

Combining all the observations in both series of experiments made at temperatures above 15° by the method of equation of conditions, we obtain the formula—

$$\eta = 0.005003 - 0.00005501\,t + 0.0000003061\,t^2.$$

which gives results in close accordance with the observed mean values, as the following comparison between the experimental and computed values shows:—

$t°$.	η.		Difference.	$t°$.	η.		Difference.
	Observed	Calculated.			Observed	Calculated.	
15.31	.004236	.004233	.000003	39.66	.003300	.003303	.000003
30.10	.004025	.004021	.000004	45.06	.003155	.003145	.000010
25.07	.003809	.003816	.000007	49.50	.003032	.003031	.000001
30.01	.003625	.003628	.000003	54.84	.002895	.002907	.000012
35.05	.003456	.003451	.000005	98 43	—	.002554	—

Surface Tension.—The superficial tension of the heptane from *P. sabiniana* was determined (1) by observations on the rise of the hydrocarbon in a cylindrical capillary tube of known diameter, and (2) by measurements of the form of an air-bubble placed under a plate of glass held under and parallel to the surface of the liquid.

In the first series of observations the apparatus was so arranged that the relation of the surface tension to the temper-

ature could be ascertained from observations on the rise of the liquid in the same tube at different temperatures. A detailed description of the apparatus is reserved for a communication giving the results of an extended series of observations on the surface tension of liquids with special reference to their chemical relations. The measurements were made by the aid of a cathetometer reading to 0.02 mm., and each result is the mean of some six or eight observations. Diameter of tube 0.2531 mm.

Temperature. °C.	Height from the outside level of the liquid to the lowest point of the meniscus in the capillary tube. Observed.	Calculated.	Difference.
7.0	49.62 mm.	49.76	+ 0.14
15.6	48.36	48.20	— 0.16
23.8	46.70	46.71	+ 0.01
30.2	45.58	45.54	— 0.04
38.4	43.99	44.05	+ 0.06
45.5	42.72	42.76	+ 0.04
54.6	41.12	41.11	— 0.01
60.4	40.10	40.05	— 0.05
69.5	38.44	38.39	— 0.05
76.8	36.99	47.07	+ 0.08

No correction has been made for the increase in the diameter of the tube with the temperature. The correction for a difference of temperature of 100° would not affect the fourth place of decimals in the value of the diameter. Combining the observations by the method of least squares, we find that the height of the liquid in the capillary tube may be accurately represented by the expression —

$$h = 58.032 - 0.1818\,t.$$

The values calculated by this formula are given in the third column of the above table.

The above formula for a tube 1 mm. in radius becomes —

$$H = 6.4581 + 0.0230067\,t.$$

If the constant of capillarity (a) be considered as half the weight in milligrams of a column of liquid, of which the area

of the base is 1 square millimeter, and of which the height is that of a column of liquid in a tube 1 mm. radius, then —

$$a = \frac{H \cdot s}{2}$$

in which s is the specific gravity of the liquid. This for heptane at 0° is —

$$a = \frac{6.4581 \times 0.70057}{2} = 2.2621 \text{ mgm.}$$

Neglecting the angle of capillarity, which, as the observations with the air-bubble show is certainly not very far from 180°, the surface tension at 0° is—

$$T = 2.2621 \times 9.81 = 22.19,$$

and its relation to the temperature is expressed by —

$$T = 22.19(1 - 0.003563\, t).$$

The observations with the air-bubble were made practically in the manner described by Quincke.* A rectangular trough 2½ inches broad, 3 inches long, and 1 inch deep, made of plane parallel plates of glass, cemented together at the edges, was levelled before the cathetometer and filled with the heptane, and another plate of glass was then immersed in the liquid to a depth of a few millimeters, and carefully adjusted until it was parallel with the surface. A bubble of air about 30 mm. in diameter was then blown under the glass by means of a bent capillary tube, and its depth (K), together with that of the point where its tangent plane was vertical (k), was determined by the cathetometer.

The value of the superficial tension in C. G. S. units is given by the expression —

$$T = \tfrac{1}{2}(K - k)^2 gs.$$

In the first set of observations ten readings of K and k were taken. The temperature was 15°.

$K = 3.622$ mm. $\qquad k = 1.083$

$g = 9.81$ " $\qquad s$ at 15° $= 0.6882$.

Hence $T = 21.80$.

* Pogg. Ann. 139, 1.

In the second set five readings of K and k were taken on another bubble. The temperature was 10°.

$$K = 3.452 \text{ mm.} \qquad k = 0.960. \qquad s = 0.6922.$$
$$\text{Hence } T = 21.12.$$

These numbers agree very well with those deduced from the height of the liquid in the capillary tube.

The method of measurement was scarcely accurate enough to afford any very reliable value of the angle of capillarity. This is given by the formula—

$$\text{Cos. } \theta = \frac{K^2}{(K - k)^2} - 1.$$

Combining all the observations, we find the angle of capillarity of heptane 167°. It is worthy of note that the heptane from *Pinus sabiniana* has the lowest surface tension of any liquid yet measured.

Since the superficial tension of a liquid entirely vanishes at the critical point, that is, at the temperature at which the gaseous and liquid states become continuous, the expression $1 - .003563t$ may afford us an approximation to the critical point of heptane, if we assume that the rate of diminution in capillarity is represented by this formula at high temperatures. We thus find the critical point of the heptane to be 281°.

Whether the heptane from *Pinus sabiniana* is absolutely identical with that boiling at about the same temperature obtained from petroleum and shale oil remains to be established. The existing evidence, so far as it goes, seems to indicate that the hydrocarbons are really isomeric.

In May 1874, Professor Schorlemmer, to whom I am indebted for a number of organic preparations for determination of certain of their physical constants, kindly sent me a quantity of normal heptane from petroleum, which he believed to be practically free from the isomeride boiling at 90°, and from octane. I found it to boil constantly between 98.1° and 99.1° under a pressure of 765 mm. Its specific gravity at 0° compared with water at 4° was 0.7299.

In May 1877, Professor Schorlemmer sent me a second sample of petroleum heptane which had been prepared with special care. This I found to boil between 98.1° and 98.6° under a barometric pressure of 750.3 mm.

A determination of its vapor-density afforded the following data:—

Weight of hydrocarbon	150.7 mgm.
Volume of vapor	91.28 cc.
Temperature	99.8° C.
Pressure	381.3 mm.

Calculated.	Observed.
49.9	50.1

Two determinations of its specific gravity at 0° compared with water at 4° gave —

I	0.7301
II	0.7301

numbers which are almost identical with that afforded by the first sample, and much higher than that of the heptane from *P. sabiniana*, viz., 0.70057.

On the other hand, the hydrocarbon from *P. sabiniana* has precisely the same specific gravity as that of the heptane obtained by heating azelaic acid with caustic baryta. Dale found that the latter body boils at 98°–99°, and has a specific gravity of 0.6851 at 17.5°; Schorlemmer, who procured the same hydrocarbon in larger quantity, observed 0.6840 at 20.5°. Reducing these observations by means of the formula given on page 160, they become respectively —

I	0.6992
II	0.7000.

If, as Schorlemmer believes, the heptanes from azelaic acid and petroleum are probably identical, the difference in their specific gravities is at present inexplicable. We are now engaged on a joint investigation on the chemical constitution of the heptane from *P. sabiniana*, which may incidentally throw light on this question.

ON THE LIQUID TOLUENESULPHOCHLORIDE.

By C. Fahlberg,

Fellow in Chemistry, Johns Hopkins University.

It is stated in an article by H. Beckurts* that a third toluene-monosulphonic acid exists in the crude mixture resulting from the action of sulphuric acid upon toluene. Although Beckurts's acid showed differences when compared with the well known toluneparasulphonic acid and the tolueneorthosulphonic acid, he neglected to prepare oxybenzoic acid from it and to prove its constitution. At the same time he gives his acid the name toluenemetasulphonic acid, and asserts that it is identical with the acid prepared by Mueller† from orthobrom-toluenesulphonic acid, by Pagel‡ from orthotoluidinesulphonic acid, and by v. Pechmann§ from paraamidotoluenemetasulphonic acid.

It was necessary to repeat his experiments for the purpose of preparing large quantities of tolueneorthosulphamide from the liquid toluenesulphochloride. In doing this my attention was directed to his article, from which I hoped to receive some benefit. On examining his method, however, I preferred for the final separation of the amides to use water instead of alcohol, to which Beckurts refers as a good solvent. My object in doing this was to avoid the changes which alcohol undergoes when an alcoholic solution is treated with bone-black as in the usual process of decoloration. With the exception of this modification I introduced no changes, but adhered strictly to Beckurts's own statements. As Beckurts's amide, fusing at 104°–105°, is more easily soluble in water than the tolueneorthosulphamide from which the separation of the former had to be effected, I could expect a separation similar to that obtained by Beckurts.

If the liquid toluenesulphochloride‖ is treated with an

* Ber. d. chem. Gesell., 10, 943.

† Ann. der Chemie, 169, 47.

‡ Ann. der Chemie, 176, 291.

§ Ann. der Chemie, 173, 202.

‖ The liquid toluenesulphochloride was cooled several times in a cooling mixture to —15°, until no more of the solid toluneparasulphochloride could be separated.

aqueous solution of ammonia and the products are allowed to cool off, there results:

I. A solution above the separated amides, consisting of an excess of ammonia, ammonium chloride, and an unknown organic substance. On evaporating this solution an oil of a dark brownish appearance separated out. Boiled with bone-black several times, fine long needles with a lustre were obtained. These needles had, after recrystallization, a constant fusing point of 186°–187°. They were found to be identical with Blomstrand's *a*-toluenedisulphamide.

II. A solid, yellowish-looking, mixed amide. This amide was subjected to a fractional solution whereby only one portion dissolved, while the other portion remained undissolved. The undissolved portion, *a*, and the dissolved portion, *b*, were treated separately.

a. This was dissolved in water, and decolorized two or three times with bone-black, when an amide separated out, fusing at 153°–154°. This amide gave pure salicylic acid, fusing at 156°, when fused with caustic potash; it was pure toluneorthosulphamide.

b. From the hot filtered solution an amide separated, fusing at 125°. This was subjected to the same operation as given under II. The undissolved portion, *α*, and the dissolved portion, *β*, were again treated separately.

α. This was dissolved in water and decolorized several times, when an amide separated out, fusing at 150°–152°. Recrystallized from pure water, the fusing point became 153°–154°. This was a second portion of toluneorthosulphamide.

β. From the hot filtered solution an amide crystallized, fusing at 120°. It was recrystallized with bone-black. The fusing point fell to 115°. Twice more subjected to bone-black and crystallization, the fusing points became 1st. 110°, and 2d. 108°. Recrystallized from pure water the fusing point did not change. This was the supposed Beckurts's toluenemetasulphamide.

For the reason that toluneorthosulphamide is very difficultly soluble in cold water, I evaporated in one portion the mother-liquors under II., and obtained from them more of Beckurts's amide, fusing this time at 105°. Some undecolorized amide in the mother-liquor caused this change in the fusing point from 108° to 105°.

In this way I succeeded in separating three amides which differed distinctly in their fusing points.

From 150 grams of liquid toluenesuphochloride I obtained: 15 grams toluenedisulphamide fusing at 186°–187°; 15 grams Beckurts's amide fusing at 105°–108°; and 100 grams toluene-orthosulphamide fusing at 153°–154°. I obtained on analysis of the amide fusing at 186°–187° the following results:

I. 0.2353 grams of the amide gave 0.4370 grams $BaSO_4$ = 0.060017 grams S = 25.50 per cent. S.

II. 0.371 grams substance gave 36 cc. N at 758 mm. pressure and 21°C = 11.00 per cent. N.

Its analysis showed it to have the composition $C_7H_{10}S_2N_2O_4$.

	Calculated.		Found.
$C_7H_{10}O_4$	158	63.20	...
S_2	64	25.60	25.50
N_2	28	11.20	11.00
	250	100.00	

I obtained on analysis of the amide fusing at 105°–108° the following results:

I. 0.2005 grams of the amide gave 0.27545 grams $BaSO_4$ = 0.03783 grams S = 18.85 per cent. S.

II. 0.3674 grams substance gave 26.80 cc. N at 759.5 mm. pressure and 19°C = 8.40 per cent. N.

Its analysis showed it to have the composition $C_7H_9SNO_2$.

	Calculated.		Found.
$C_7H_9O_2$	125	73.11	...
S	32	18.71	18.85
N	14	8.18	8.40
	171	100.00	

I obtained on analysis of the amide fusing at 153°–154° the following results:

I. 0.2015 grams of the amide gave 0.2747 grams $BaSO_4$ = 0.037725 grams S = 18.72 per cent. S.

II. 0.39765 grams substance gave 28 cc. N at 763 mm. pressure and 16°C = 8.21 per cent. N.

Its analysis showed it to have the composition $C_7H_9SNO_2$.

	Calculated.		Found.
$C_7H_9O_2$	125	73.11	...
S	32	18.71	18.72
N	14	8.18	8.21
	171	100.00	

It is evident from these analyses that the amide fusing at 186°–187° is a toluenedisulphamide, while the amides one of which fuses at 105°–108° and the other at 153°–154° are toluenemonosulphamides, the latter being the well-known toluneneorthosulphamide.

After having concluded the oxidation of the toluneneorthosulphamide upon which a short article by Professor REMSEN and myself has been published*, I proceeded to oxidize the amide fusing at 105°–108°.

The results reached by the oxidation were found to be contradictory to the statements made by Beckurts. The amide fusing at 105°–108° became oxidized in the same way as described in the paper on the oxidation of toluneneorthosulphamide, in which the permanganate of potassium was the agent used. The oxidized solution was evaporated to $\frac{1}{3}$ or $\frac{1}{4}$ of the original volume. Before the addition of hydrochloric acid, the solution tasted sweet, reminding one of the anhydroorthosulphaminebenzoic acid. With the possibility in view that anhydroorthosulphaminebenzoic acid might be present, I proceeded to a careful investigation of this solution. On adding hydrochloric acid, parasulphaminebenzoic acid was precipitated and proved beyond a doubt to have the same properties as the acid produced from pure tolueneparasulphamide. The paraoxybenzoic acid which was prepared from it fused at 210°. The filtered solution from parasulphaminebenzoic acid was evaporated to dryness and the residue treated with alcohol. From the alcoholic solution there was obtained a substance in every respect identical with anhydroorthosulphaminebenzoic acid. The salicylic acid produced from it fused at 156°. That part of the residue which was undissolved by the alcohol was found to contain the acid potassium salt of orthosulphobenzoic acid and potassium chloride; the former when fused with caustic potash gave salicylic acid fusing at

* Ber. d. chem. Gesell., 12, 469.

156°, just as in the case of anhydroorthosulphaminebenzoic acid. Since we know only one oxidation product from toluneparasulphamide and two oxidation products from toluneorthosulphamide, Beckurts's amide fusing at 105°–108° corresponded, according to this experiment, to a mixture of toluneparasulphamide and tolueneorthosulphamide. The products of this oxidation mentioned above are: parasulphaminebenzoic acid, anhydroorthosulphaminebenzoic acid and acid potassium orthosulphobenzoate. There was nothing left to support the belief in the existence of Beckurts's toluenemetasulphamide. An experiment which I undertook afterwards convinced me conclusively of the correctness of my view.

Equal portions of pure toluneparasulphamide (fusing at 136°) and pure tolueneorthosulphamide (fusing at 153°–154°) were dissolved in water and subjected to fractional crystallization. Neither of these amides could be separated from the other, but constant fusing points were noticed indicating a tendency to crystallize together. I noted the fusing points 120° and 108° as the most stable. The mixed amide fusing at 120° crystallized in long, fine needles, while the mixed amide fusing at 108° crystallized in needles and small leaves; for the latter Beckurts gives a similar statement. Slight impurities lower the fusing point to 104°–105°, or even below that.

In conclusion I would state that Beckurts's toluenemetasulphamide fusing at 104°–105° was found to be a mixture of toluneparasulphamide and tolueneorthosulphamide. This corresponds with the oxidation phenomena and its formation from pure toluneparasulphamide and tolueneorthosulphamide.

The amide fusing at 186°–187° was found to be identical with Blomstrand's *a*-toluenedisulphamide. The occurrence of toluenedisulphonic acid in the crude mixture, resulting from the action of fuming sulphuric acid upon toluene, is interesting in this respect. It was shown by C. Senhofer* that the introduction of a second sulpho-group into toluene presents difficulties, and that only a mixture of anhydrous phosphoric acid and fuming sulphuric acid accomplishes this result satisfactorily. C. W. Blomstrand†, who undertook a similar investigation, heated toluene with fuming sulphuric acid at 160°, and obtained two different toluenedisulphonic acids, of which

*Ann. der Chemie, 164, 126. †Ber. d. chem. Gesell., 5, 1084.

neither was identical with the acid obtained by C. Senhofer. It is difficult to say how the toluenedisulphamide from the liquid toluenesulphochloride was overlooked. The only explanation would be that no one knew the properties of the toluenedisulphamide, there being no statements on that subject published. This *a*-toluenedisulphamide is very soluble in an ammoniacal solution; it is therefore only found in the solution, and not with the separated toluenemonosulphamides when toluenesulphochloride is treated with an aqueous solution of ammonia, as in the usual formation of amides. It is a singular fact that the toluenedisulphochloride is found again with the liquid and not with the solid toluenesulphochloride, when the two are separated in the way described at the outset. According to Blomstrand's statement the *a*-toluenedisulphochloride is a solid body fusing at 51°–52°. In the course of this investigation, however, it became apparent that not only *a*-toluenedisulphochloride, but also toluneneparasulphochloride is soluble in the liquid toluneorthosulphochloride at —15°.

I am at present engaged in the oxidation of toluenedisulphamide, upon which I hope to report as soon as the investigation is concluded. *a*-Toluenecyanide has also been prepared from *a*-toluenesulphonate of potassium and potassium cyanide, and will be studied in connection with the oxidation of toluenedisulphamide. In preparing toluenedisulphamide I made use of a reaction by which from the solid toluenesulphochloride and concentrated or fuming sulphuric acid, toluenedisulphonic acid was readily obtained in almost theoretical quantity; this proved to be the same acid from which the amide fusing at 186°–187° was derived.

The method consists in heating both substances together, when the reaction takes place as follows:

$$C_6H_4\begin{cases}CH_3\\SO_2Cl\end{cases} + SO_4H_2 = C_6H_2\begin{cases}CH_3\\SO_2OH\\SO_2OH\end{cases} + HCl.$$

It is possible that a third sulpho-group may be introduced in this way and that other aromatic compounds may give analogous results. This investigation, however, I shall postpone for the present.

BALTIMORE, *May 8th*, 1879.

ON THE PRODUCTS OBTAINED BY THE NITRATION OF METACHLORSALICYLIC ACID.

By Edgar F. Smith and Gertrude K. Peirce.

Metachlorsalicylic acid was prepared by the introduction of a calculated amount of pure dry chlorine gas into an alcoholic solution of salicylic acid. From the dichlor-acid, which was invariably produced in rather large quantities, it was separated by means of the barium salt, the latter being much more soluble than the corresponding derivative of the above acid. Frequently glacial acetic acid was employed to dissolve the salicylic acid, but as in this case there was usually an abundance of decomposition products produced, alcohol was substituted for the same.

Metachlorsalicylic acid was first obtained by Huebner and Brenken,* studied later by Rogers,† and also by one of us.‡ In a pure condition the acid forms beautiful, long, colorless needles, readily soluble in water. It fuses at 172°C.

The first notice we have observed regarding the nitration of this acid was that of Rogers.§ He obtained from it monochlordinitrophenol and a nitro-acid fusing at 151°C. His mode of forming the latter derivative was to mix the chlorsalicylic acid with glacial acetic acid and to the warmed solution add small quantities of fuming nitric acid from time to time. When the solution had stood for some time and was cool, a rather large quantity of water was poured into it, causing the separation of the greater portion of the nitro-acid.

Our plan of nitration was simply to add small quantities of the metachlor-acid gradually to fuming nitric acid in a medium-sized flask—shaking the latter constantly to aid the solution, and finally applying a gentle heat upon a water-bath. To the cold nitric acid solution water was added. A light yellow-colored mass immediately separated and was filtered, washed

* Ber. d. chem. Gesell. 6 (1873), 174.
† Inaugural Dissertation, Goettingen (1875).
‡ Ber. d. chem. Gesell. 11 (1878), 1227.
§ Dissertation.

imperfectly with cold water and then boiled with an aqueous solution of potassium carbonate. The solution, after filtration and evaporation, was permitted to stand for some time. Long, deep red colored needles rapidly appeared. These were filtered off and farther examined. For convenience we would designate this crystalline mass A. From the filtrate upon farther evaporation there separated a mass of dark red colored nodules which, for the time, we will consider as B.

Examination of Product A.

This portion was redissolved and recrystallized slowly from an aqueous solution. The same needles appeared, and by filtering these before the solution had cooled, again evaporating and allowing to cool, to our surprise there appeared quite a different salt, forming bundles, consisting of orange-colored needles. Both the latter and the long red-colored needles were recrystallized and subjected to farther examination.

*Salt crystallizing in long red Needles.** — *Analysis.* — .1691 grams salt, dried at 130°C, were placed in a platinum crucible, a few drops of concentrated sulphuric acid added and a gentle heat applied. The residual K_2SO_4 = .0264 grams, which corresponded to 15.60 per cent. K. The salt does not possess water of crystallization. The calculated amount of K in potassium monochlordinitrophenol is 15.23 per cent. There was, therefore, no doubt as to the constitution of this compound.

The free acid derived from this salt crystallized from aqueous solutions in long yellow needles, which fused at 80°C and solidified again at 69°C. It is also identical with the phenol of Rogers (see above) and the alpha-monochlordinitrophenol of Faust and Saame.†

Salt crystallizing in orange-colored Needles. — *Water Determination.* —.1617 grams air-dried salt lost upon heating at 140°C for a number of hours .0168 grams H_2O = 10.39 per cent.

1½ molecules water require 9.53 per cent.

Potassium Determination. —.1449 grams dried salt gave upon evaporation with sulphuric acid .0480 grams K_2SO_4 = 14.86 per cent. K. From this analysis we observe that this salt too

* Proceedings Am. Phil. Soc. June 21, 1878.

† Ann. der Chemie (1870), 7 Supplement Band, 174.

is a derivative of a monochlordinitrophenole. The formula would be $C_6H_2Cl(NO_2)_2OK + 1\frac{1}{2}H_2O$.

This salt is much more soluble than the red. The color of the latter is so intense as to obscure the yellow, which consequently is overlooked unless great care is exercised in the purification of the red-colored compound.

Upon mixing an aqueous solution of this yellow salt with dilute hydrochloric acid, the corresponding phenol separated in yellowish-colored masses, which were recrystallized repeatedly from aqueous solutions, when long orange-colored needles appeared. The fusing point of this acid remains constant at 79°–80°C. The point of solidification was at 25°C, considerably lower than that of the acid corresponding to the red salt. In cold water the acid is rather insoluble, readily dissolved on applying heat.

Another noticeable difference in the above described phenols is in the silver salts. The alphachlordinitrophenol yields a soluble silver salt crystallizing in long bright red colored needles; the isomeric compound just mentioned above one which separates in bronze-colored needles, possessing a marked metallic lustre.

As the second phenol was formed in small quantities it was almost impossible to subject it to as thorough investigation as would seem desirable. The material, however, which was examined was thoroughly pure, and as the same analytical results were repeatedly obtained, the conclusion is that it is another of the many compounds having this composition.

Analysis:

.512 grams substance gave .6210 CO_2 = .1693 C = 33.06 per cent. C; and

.062 grams H_2O = .0068 H = 1.32 per cent. H.

Calculated, C = 33.00 per cent. and H = 1.37 per cent.

Examination of Product B.

The dark red nodular crystals constituting the second product obtained in the nitration were crystallized repeatedly from water. The salt continued to grow lighter in color and at the same time assumed a more sightly form — presenting long, light yellow-colored needles, aggregating in fan-like masses with a satiny lustre.

The acid derived from this salt was light yellow in color, forming rather short, strong needles, exhibiting light refraction. When pure the constant melting point was discovered to be 162°–163°C. Very readily soluble in water.

Undoubtedly this is the acid described some years ago by Huebner.* Rogers, too, probably had it in an impure condition. He mentions in his dissertation that he obtained an acid fusing at 168°C, and inferred that it was a probable isomer of the monochlornitrosalicylic acid which principally engaged his attention. Yet throughout our entire work we never discovered the slightest trace of an acid with a fusing point of 151°C. Our impure acid frequently fused about this temperature, but one or two recrystallizations were invariably sufficient to raise it to 162°–163°C.

Nothing more was done with the acid. Our attention was now directed to the formation of a few derivatives with a view of ascertaining how widely they differed from those of the supposed isomeric acid of Rogers.

Potassium Metachlornitrosalicylate. — $C_6H_2Cl^mOH^cNO_2COOK$.

Obtained by boiling the acid with a slight excess of potassium carbonate. Repeated recrystallization gave us the pure salt in aggregated needles with a beautiful satiny lustre. The salt yields a very bitter, disagreeable taste when placed upon the tongue. Very soluble in water. It is anhydrous.

Potassium Determination.—0.4872 grams of thoroughly dried salt treated with sulphuric acid gave, upon evaporation, 0.1623 grams potassium sulphate = 14.95 per cent. K.

Calculated, 15.34 per cent. K.

Barium Metachlornitrosalicylate.— $(C_6H_2Cl^mOH^cNO_2COO)_2Ba$.

By boiling the aqueous solution of the acid with an excess of barium carbonate the salt was formed and crystallized in dark orange-red colored needles, which were very insoluble and exceedingly difficult to obtain pure. It appears to have water of crystallization, but on drying in the air rapidly loses the same. An analysis was made of the dried material.

* Jahresbericht (1866), 349.

Barium Estimation.—0.2808 grams salt gave with sulphuric acid .1188 grams $BaSO_4$ =24.70 per cent. Ba.

Calculated, 24.03 per cent.

The silver salt formed a light brown colored powder, which was placed in a tube of Bohemian glass, an excess of ethyl bromide added, the tube sealed and heated for several hours in a water-bath, and in this manner we obtained

Ethyl Metachlornitrosalicylate, $C_6H_2Cl^m OH^o NO_2 COOC_2H_5$,

which, when crystallized from an alcoholic solution, formed almost colorless flattened needles, fusing at 89°C. A very strong light refraction was shown by the crystals.

Upon heating a portion of the ether with an excess of alcoholic ammonia we obtained

Metachlornitrosalicylamide, $C_6H_2Cl^m OH^o NO_2 CONH_2$,

a brick-red colored compound forming small nodular crystals readily soluble in alcohol, more difficultly soluble in water. The fusing point is constant at 199°C.

Upon comparison with Rogers' work it will be found that our results are quite different, and this would indicate that two nitro-acids are formed when metachlorsalicylic acid is nitrated.

Our work in this direction has been discontinued, inasmuch as we have received information that the investigation of the acid has been almost completed by another party.

Another interesting compound which was obtained by us is the following combination of alpha-monochlordinitrophenol with aniline:

Alpha-Monochlordinitrophenol Aniline.

$C_6H_2Cl(NO_2)_2OHC_6H_5NH_2$.

By mixing a small quantity of the phenol with sufficient aniline to dissolve the former in the cold, a beautiful deep red colored liquid was procured. A drop of this solution placed upon the skin imparted to the latter a rather difficultly removable stain. On evaporating the colored liquid upon a water-bath in a large open dish and allowing the same to cool, hard

nodular crystals separated, which were well pressed between paper and dried by exposure to the air. From aqueous solutions the compound is obtained in long, curled, light yellow colored masses. It fused constantly at 137°C. Aniline will separate upon boiling its aqueous solutions violently. An analysis of the substance showed it to be a union of one molecule phenol with an equal amount of aniline.

Analysis.—0.1221 grams dried substance burned with lead chromate gave .0188 grams carbon = 46.19 per cent. C, and 4.00 per cent. H. The theoretical percentages required are 46.22 per cent. C and 3.21 per cent. H.

UNIVERSITY OF PENNSYLVANIA, *May 3d*, 1879.

ON GLYCOCHOLIC ETHER.

BY ALFRED SPRINGER.

While engaged in experiments upon different ethers, it occurred to me that those of the acids commonly contained in bile, especially glycocholic and taurocholic, might be interesting. Since ox-gall is easily obtained, and its composition is tolerably well known, I chose that for my starting point.

At a first glance it would seem as if the etherification need require but little labor or time; nevertheless, any one who has ever experimented upon these acids can readily understand the difficulties which must be surmounted in order to avoid working with their decomposition products.

My first attempt at the preparation of glycocholic ether was as follows: After having extracted a quantity of sodium glycocholate from about twenty ox-galls, this salt was taken with a sufficient quantity of sulphuric acid and alcohol and distilled in a small glass retort. Only ethylic ether and alcohol passed over into the condenser. In the retort there remained a brownish-yellow resinous substance, insoluble in water and but partly soluble in alcohol or ether, which I found

upon examination to consist mainly of dyslysin mixed with choloidic and cholonic acids. A similar experiment made with hydrochloric instead of sulphuric acid gave equally unsatisfactory results.

I next prepared an alcoholic solution of the sodium salt, and passed dry hydrochloric acid through it for twenty-four hours, but still could obtain no ether. After this I placed in two strong glass tubes mixtures of hydrochloric and sulphuric acids respectively with alcohol and the sodium glycocholate, sealed them hermetically, and heated for four days on the water-bath. A thick resinous mass was formed, which again proved to be mainly dyslysin.

It is not unfrequently the case that an acid as such has a much greater affinity for etherification than a salt wherefrom the acid is liberated during the process. I have often observed that butyric ether made from sodium butyrate has neither so pure an odor nor taste as that prepared from butyric acid directly, although the same salt had been used as the starting point for both preparations. The same thing holds true with valeric ether also. These facts led me to try glycocholic acid in an isolated state instead of the salt with which I had been working.

Eighty ox-galls, fresh from the gall-bladder, were evaporated almost to dryness on the water-bath, and the residue was exhausted with alcohol. The alcohol was next distilled off, and the substance remaining in the retort was diluted with water and treated with milk of lime. To the filtered and cooled liquid, which had a faint wine color, dilute sulphuric acid was added until a permanent turbidity was produced. Soon the solution solidified forming a mass of crytals, which were again dissolved in water and the process of purification repeated. At last I obtained nearly a pound and a half of beautiful white needles of glycocholic acid.

These crystals, distilled with alcohol and sulphuric acid, showed no more inclination to form an ether than the sodium salt. But when they were heated with hydrochloric acid and alcohol in a sealed tube, an ether began drop by drop to form; until at the end of two weeks all the crystals had disappeared, and the ether collected upon the surface of the liquid in their stead. Later I discovered that this ether could be obtained more easily if the glycocholic acid was first dis-

solved in alcohol and dry hydrochloric acid passed twenty-four hours through the solution. This solution, heated in a sealed tube with alcohol and hydrochloric acid, became thoroughly etherified in two days. As the pressure within the tube was enormous, the usual precautions had to be taken against the danger of explosion. Since the ether was lighter than the other liquids in the tube it was easily taken off from the top.

The color of the ether is dark brown. Thinking that decolorization might be possible I tried to distill the substance, but found that it decomposed. Its specific gravity is 0.901. When exposed to the open air it decomposes, leaving a white resinous mass. In a closed vessel it may be kept for any length of time, and in a sealed tube it may be heated to a quite high temperature without suffering decomposition. Water acts upon this ether somewhat strangely. At first the mixture becomes thick and brown, as if it were dyslysin; but gradually it whitens, and crystals of glycocholic acid are deposited. The only way the ether could be washed was with hydrochloric or sulphuric acid.

During my experiments eighteen combustions were made of this ether and its educts. I need give the results of only one analysis. The nitrogen was determined by Constance Makris's modification of the Will-Vanentrapp process; a method which gave me extremely satisfactory results. The figures obtained agree very well with the formula $C_{26}H_{42}(C_2H_5)NO_6$.

	Theory.	Found.
Nitrogen, ...	2.84	2.89
Carbon, ...	68.15	67.23
Hydrogen, ...	9.53	9.40
Oxygen, by difference, ...	19.48	20.48
	100.00	100.00

Since the foregoing was written I have prepared several new ethers, namely, choloidic ether from ox-gall, and hyoglycocholic and hyotaurocholic ethers from pig-gall. I have these ethers in a pure condition, and have determined some of their reactions; but I prefer not to publish any detailed account of them until I have completed my analyses and definitely ascertained their formulæ.

CINCINNATI, *April* 1879.

REVIEWS AND REPORTS.

Brief Review of the most important Changes in the Industrial Applications of Chemistry within the last few Years.

(*Continued from page 66.*)

Metallurgy — Continued.

Nickel and Cobalt.—Within a decade the extraction of these metals has increased notably in importance; and the scale upon which they are worked has expanded greatly in consequence of their successful application in electroplating, while formerly nickel was scarcely used save in its alloys of the German-silver class, and metallic cobalt was not in industrial use at all. Extensive search has been made in various countries for new supplies of ore, in the main resulting in bringing together small lots from different sources. Probably the most important single new locality is New Caledonia, furnishing, not the more common sulphides and arsenides, but the hydrous silicate of nickel and magnesium known as Garnierite or Noumeite. The metallurgical processes in use are carried out partly in the "dry" and partly in the "wet way." In the former direction there has been improvement, the result of experience, in the concentration of poor ores, such as nickeliferous pyrites, to mattes containing a much increased percentage of nickel, and the cobalt which may be present can be recovered in the state of oxide, to be subsequently reduced to metal, instead of obtaining it merely in the form of crude silicate, as "smalt" or "zaffre." The metallic nickel furnished to commerce is of higher purity than was known a few years ago, 98 or 99 per cent. of real nickel being easily obtainable, and even higher grades of product seen to some extent. Moreover, the small, irregular grains and the cubes of but half-melted nickel which not long ago constituted the only forms in which the metal was turned out, have been largely replaced by solid ingots of various weights up to 5 or 6 kilos each, cast from crucibles in which, with the aid of well-arranged wind furnaces, the refractory metal has been completely fused.

Zinc.—The most noteworthy increase in the production of zinc of late years has occurred in the United States (New Jersey, Pennsylvania, Virginia, Tennessee, Illinois, Iowa, Wisconsin, Missouri), which may now be reckoned among the great sources of the world's supply.

The methods now and for a long time in use for the extraction of this metal from its ores still leave much to be desired; the various forms of distilling apparatus are complicated, more or less troublesome, and not adapted to continuous working; and much zinc is obtained as oxide by the burning of the metallic vapor in contact with air, or is deposited in a pulverulent form by too sudden cooling instead of condensing to liquid metal fit for casting into ingots. None of the attempts which from time to time have been made to devise a furnace capable of turning out, without serious loss, fused zinc by a continuous process, seem yet to have achieved success. The nearest approach to such success has been the continuous reduction and distillation of the metal with intentional combustion of the vapor, to produce zinc white for painter's use. It may possibly be worth consideration and experiment whether the volatilization of zinc might not be, at least to a large extent, prevented by reducing, under suitable conditions of temperature and furnace atmosphere, its ores along with those of lead, taking advantage of the fact, illustrated by the ancient method of making brass from copper heated with calamine and charcoal, that the presence of the less volatile metal in the alloy reduces notably* the volatility of the other; the subsequent separation of zinc and lead admitting of being effected, as far as much the larger portion of each metal is concerned, by liquation, as in the now common Parkes' process for desilverization of lead. If such a reduction method could be given practical shape, any zinc vapor which did still escape might be allowed to burn and collected as zinc oxide for painting.

Tin.—The most prominent fact for some time past in the history of this metal has been the very large addition to our annual supplies since 1870 coming from Australia, while the product from the Dutch East Indies has also largely increased. The tin-bearing territory of New South Wales and Queensland covers several thousand square miles, affording already some ore from veins likely to be much more largely opened up in the future, but much larger quantities from magnificent washings of stream tin. Tasmania also affords some smaller additional supply. Most of the Malay tin of Banca, Billiton, the peninsula of Malacca, &c., comes from "dry diggings" in decomposed granite or pegmatite, the more or less disintegrated remains of felspar and quartz being washed away, and the ore smelted on the spot in rude furnaces of small size with charcoal fuel, and a blast from the hollow trunk of a tree in which a piston works to and fro. Twelve or fifteen years ago the general supply of the world might have been set down in round numbers as—

* It would have to be determined by experiment how far lead can thus give fixity to zinc at the temperature necessary for the reduction of both and separation of slag.

	Metallic Tin.
From England (Cornwall and Devonshire).....	8,500 tons.
" Malacca and the Malay Islands.....	7,500 "
" Saxony, Bohemia, and all other sources..	450 "
	16,450 tons.

A similar estimate for the present time stands thus:

From Malacca and the Malay Islands.....	14,500 tons.
" Australia	10,000 "
" England (Cornwall and Devonshire) ...	9,500 "
" Saxony, Bohemia, Bolivia, &c., &c.,....	650 "
	34,650 tons.

This doubling of production has been attended with a corresponding fall in price—from £127 to £61 per ton.

There has been no material change in the simple processes of tin-smelting. The application of Oxland's method of preparing the ore by getting rid of accompanying wolfram in the form of sodium tungstate has furnished some material for the utilization of tungsten compounds; most of the latter, however, so far as in use at all, are obtained from independently mined or mechanically separated wolfram.

Bismuth.—At the chief seats of bismuth production in Saxony and Bohemia, the old and simple process of extraction of the native metal from rock through which it is disseminated, by liquation in slightly inclined cast-iron tubes, has been abandoned, it being found that too much of the now quite valuable metal was left in the residues of imperfectly exhausted gangue. Instead, the mixed ores, largely associated with those of cobalt, are roasted and then reduced in the furnaces of the smalt-works with additions of charcoal, metallic iron and slag. Two layers separate after fusion, the upper one consisting of cobalt-speiss (arsenides of cobalt, nickel and iron), the lower of crude metallic bismuth. The latter is run off in the still fluid state after the former has solidified, and the bismuth, cast into blocks, is refined by eliquation at a gentle heat on an inclined iron plate. Almost pure bismuth flows off, while the foreign metals with a little bismuth remain as dross to be worked over.

To a limited extent the ores of this metal have of late years also been worked in the wet way—as at Meymac in France, where a small supply of oxidized ore is treated by solution in hydrochloric acid and precipitation by water or on bars of iron.

There has been a remarkable increase of demand for bismuth within a few years, leading to increase of price,

since although supplies of ore have been received from several new quarters, chiefly Peru and South Australia, in less quantity from Mexico, France, &c., the aggregate of these new receipts has borne but a small proportion to the amount furnished by the one long known and most important mining region of the Erzgebirge, of which Schneeberg in Saxony and Joachimsthal in Bohemia may be considered the two chief points. At present the annual supply is estimated as —

From Saxony and Bohemia, . . .	32 tons
From all other sources, ...	3 "
	35 tons

of which much the largest part is devoted to the production of bismuth oxychloride and hydrato-nitrate for use in medicine and as cosmetics, most of the rest being employed in making readily fusible alloys and producing the shell-like lustre on porcelain which has given rise to the name "porcelaine nacre."

Copper.—Amongst the countries which have added most to the general supply of copper for the last quarter of a century are Chili and South Australia; the mines of the former have of late increased, those of the latter diminished in productiveness. To these will probably erelong deserve to be added Arizona, where valuable ores are abundant, and possibly at some later day Northwestern Texas. The product of the Lake Superior region has assumed an important place.

The general course of copper-smelting has undergone no great change for a long time, though there have been local variations of practice, due chiefly to special supplies of ore requiring particular treatment, and to the establishment of new seats of the industry. Swansea no longer fully holds the position of supremacy it formerly enjoyed, but the tendency is still marked toward the concentration of ores, and, of late years, of mattes and crudely smelted regulus of copper, at this and a moderate number of other centres, there to be treated with all the advantages of skilled labor, suitable and abundant fuel, &c. The most remarkable proposal of a new method of furnace treatment is that of Mr. Hollway, very recently brought before the Society of Arts of London, looking to the application of the Bessemer blast of air to sulphides in a melted state, the temperature being maintained simply by addition of fresh quantities of ore. Too little is yet known of the results even of such experiments as have been made for an opinion to be formed of the probable value of the idea; some advantages at once suggest themselves, but there are also manifest difficulties, such as the effect of the presence of much silica and the risk of loss by volatilization.

Relatively, much greater extension of processes in the liquid way has occurred of late years than has characterized the furnace methods. The very large use now made of the sulphur of more or less cupriferous pyrites in the manufacture of sulphuric acid has furnished abundant material, and the saving of the copper contained in burnt pyrites residues has become a regular subsidiary industry, especially in England, where in 1875 no less than 9600 tons of the metal were thus produced, several thousand pounds' worth of silver and gold being also obtained from the same source. The main features of the process consist in calcination of the spent pyrites mixed with common salt in furnaces often heated by gaseous fuel from a Siemens generator, leaching with water, and precipitation by metallic iron, preferably used in the spongy state obtained by reduction of some of the exhausted pyrites in a muffle furnace with ground coke.

In the United States the introduction of the Hunt and Douglas wet process should be particularly noticed — its wide range of applicability to ores of different kinds is one of its prominent merits. The material to be treated, roasted at a gentle heat if necessary to remove sulphur or decompose carbonate, is exposed to the action of a mixed solution of ferrous chloride and sodium sulphate and chloride,* this being used either cold, or, with a view to more rapid effect, in a heated state; the undissolved residue is washed with a further portion of the same solution (hot); and from the mixed liquids obtained the copper is thrown down by metallic iron, reproducing the original solvent to be used over again. Taking only the case of the copper present as cupric oxide in the roasted ore, the reactions are essentially,

$$3CuO + 2FeCl_2 = Cu_2Cl_2 + CuCl_2 + Fe_2O_3$$

the cupric chloride dissolving of course in the water used, while the cuprous chloride is rendered soluble by the presence in the liquid of ferrous and sodium chlorides, and

$$CuCl_2 + Cu_2Cl_2 + Fe_2 = Cu_3 + 2FeCl_2.$$

This method has been successfully used with copper ores (simply), both of the oxidized and sulphurous classes, and also with ores containing the precious metals, these latter being obtainable from the residues after the copper has been removed by leaching.

The more careful examination which submarine telegraphs have led to of the great influence upon the conducting power of copper wire for electricity of impurities occurring to even a very minute extent, has stimulated the production of much

* Obtained by the addition of common salt in excess to solution of ferrous sulphate.

purer copper than could readily be had ten or twenty years ago, and hence copper refining has assumed an increased degree of importance and commands increased attention and care.

Lead.—Among the greatest recent additions to the sources of supply of this metal must be counted the argentiferous and auriferous lead ores of the Rocky Mountains and outlying ranges to the eastward of the Sierra Nevada, especially in Colorado, Utah and Nevada, where galena and cerussite have been discovered and worked upon the grandest scale, the precious metals present often causing the lead to assume but secondary importance, while in the aggregate this latter possesses immense value. The same regions, speaking broadly, afford also vast quantities of iron and copper pyrites, and zinc blende; from the working of these for gold and silver much copper is saved, chiefly in mattes to be worked over elsewhere, while the great bulk of the zinc is lost.

In connection with the working of these ores, though of course applicable to and in practice applied to those of various other kinds, may be noted as capital improvements in mechanical treatment the use of the "Blake Crusher," the invention of Eli W. Blake of New Haven, Conn., for breaking down the ore to small fragments, the steady mastication effected by which is in marked contrast with the slow and power-consuming work of the old-fashioned crushing rolls; as also the substitution, for reduction of the crushed ore to powder, of stamp batteries made wholly of iron, with well proportioned and well finished parts, for the more clumsy constructions, partly of wood, which were formerly in use. Direct-acting, steam-driven stamps have also been brought into use, but to no large extent on account of their greater liability to need repairs at the hand of the skilled machinist, not always available in rough mining regions. Many valuable contrivances for the dressing and concentration of ores have also been added to the older arrangements.

In the chemical treatment of lead, as well as other ores, improved forms of roasting furnaces have proved of much value, particularly those of the type represented by the Gerstenhœfer and Stetefeldt furnaces, in which finely pulverized ore is fed in at the top of a red-hot shaft of fire-brick, down which it drops, encountering on the way an upward current of highly heated gases, partly the products of combustion from the fireplaces, but including an abundant supply of surplus atmospheric oxygen. These more modern furnaces have in a measure taken the place of the simple reverberatory for roasting, while for smelting the roasted ore this latter has also to a considerable extent been supplanted by small blast furnaces, in the construction of which hollow cast-iron walls traversed by a current of water—water-jackets—are coming into more

general use than formerly, replacing the fire-brick linings, which in some regions are procurable only from a distance and at heavy cost. The very general introduction of processes for desilverization, although of primary consequence in relation to the saving of the precious metal, has resulted also indirectly in softening and improving the character of the average lead of commerce.

Mercury.—As regards the supply of this metal, for which the demand has been greatly extended by the expansion of gold and silver mining within the last thirty years, the great fact has been the discovery of Californian cinnabar* upon a scale placing the United States first amongst the countries producing mercury, while not inconsiderable though irregular supplies have also been received from Borneo. The present annual production may be set down in round numbers as—

From California.....	2353	tons (of 2240 lbs).
" Spain (Almaden).....	1424	"
" Austria (Idria)	273	"
" all other sources.....	263	"
	4323	tons.

The metallurgy of mercury still continues in a very unsatisfactory condition, the loss being enormous, while the low price at which alone the metal can now be sold ought to prove a stimulus to more economical management of the reduction. At present it is estimated that the best results are obtained at Idria, where nevertheless the loss is 30 per cent. on the amount of metal shown by assay to be present; in California there is an average loss of something like 40 per cent., while at Almaden in Spain it is set down as 50 to 53 per cent. To this immense waste must be added the large quantities afterwards lost in use, gold and silver amalgamation processes involving the sweeping down to the rivers of very much finely-divided mercury and its compounds, never to be recovered by any practically available means.

The chief sources of loss in reduction are, first, imperfect heating of the larger fragments of cinnabar-bearing rock, so that portions of ore remain unacted on in the interior; and, second, imperfect condensation of the vapor, which escapes from cracks and defective joints of the furnaces and passes through the porous masonry of their walls. The latter of these causes of loss is the more serious in the extent of its results. Attempts to obviate it, such as that made many years ago in the Palatinate under the direction of the late Dr. Ure, by

* Cinnabar, accompanied as usual by small quantities of native mercury, occurs at sundry points not only in California, but northwards in Oregon, Washington Territory and Idaho. The deposits which up to the present have proved practically important are confined to the first named State.

using vapor-tight retorts of cast-iron heated from the outside and retaining the sulphur by means of lime, involve increased difficulty from the first mentioned cause, since the heat has to penetrate the semi-diameter of the retort as a whole, and the volume of material heated is swollen by the addition of the lime, while no heat is obtained from the combustion of the sulphur. The same remarks apply to the bell-furnaces of Bohemia, in which reduction is effected by means of iron or "Hammerschlag." Using such arrangements with poor ores—and the great mass of the ores usually available are poor—the consumption of fuel is extravagantly large, and the iron vessels are rapidly destroyed, or much cinnabar escapes reduction. In the brick-work furnaces used at all the most important seats of mercury production the sulphur is burned off by the oxygen of the air, producing much of the necessary heat, though Californian experience seems to have shown that there may be an unwise economy of outside fuel, it being well to supply by means of such fuel burned in separate fireplaces adjoining the hearth space occupied by the ore, ample heat to ensure the thorough expulsion from the rock of all mercuric sulphide. The great difficulty, however, arises from the escape of uncondensed vapor of mercury, the masonry and the underlying soil bearing ample testimony to this in the large quantities—thousands of pounds sometimes—of irregularly condensed metal found soaking through the porous material when old furnaces are taken down.

The most hopeful line of improvement seems to be that of a combination of all the safeguards which have individually proved more or less efficacious, along with perhaps some others which may be suggested, small in themselves, but likely to prove useful in detail, say some such general arrangement as the following: 1st, detached fireplaces, with grates adapted to the combustion of the fuel used, delivering their gaseous products of combustion into — 2d, hearths for the reception of the properly piled ore, to be constructed of an outer shell of cast-iron plates put together with planed flanges and screw bolts, or else of heavy riveted boiler-plate, made as vapor-tight as possible, with a thick interior lining of fire-brick; 3d, a first set of condensing flues leading from the hearths, also of heavy cast-iron, brick-lined only so far as the high temperature extends, with sufficient number of such flues and subdivision of cross-section to give extensive cooling surface; 4th, a second set of flues, extensions of the first, of stout Russia sheet iron, well asphalted inside and out by immersion at a temperature just short of redness in boiled coal tar, to resist the corrosive effect of the sulphur acids formed; 5th, a system of pipes for the injection of cold water spray into the condensing flues, and well-arranged drip-pipes to carry off *promptly* liquid water and condensed mercury; 6th,

an effective exhauster to produce forced draught through the flues irrespective of the temperature within them, and to prevent the tension of the contained gases ever exceeding the atmospheric pressure without. The same set of condensers might be worked with several fireplaces and hearths if intermittent firing be practiced, but with detached fireplaces it does not seem difficult to provide for continuous working by means of well-fitted and vapor-tight doors to the hearths for the discharge of burnt out ore and the introduction of fresh.

Silver.—In this country it is needless to more than refer to the immense additions to the world's stock of silver which Nevada, Colorado and other far Western States have made within twenty years, treasure comparable with and even exceeding the flood-tide from Spanish America in its period of greatest prosperity. In Europe the importance of the results obtained and their influence on present problems of finance and political economy, seem scarcely to be well understood by the general public, though no doubt familiarly known to many of those who concern themselves about such questions.

In various mining districts of the world, but notably in this region of new and great activity in the United States, there have been modifications in all three of the classes into which the processes for reducing silver from its ores may be divided.

1. *Amalgamation processes, involving the collection of the silver, however first reduced, by solution in mercury.*

Certain ores are found to be adapted to immediate amalgamation, while others cannot be thus profitably worked unless first roasted, either alone or more usually with an addition of common salt in order to produce silver chloride. For the purpose of this roasting, as with other like objects in view in the treatment of the ores of other metals above alluded to, new forms of furnaces, such as the Stetefeldt, have come into use, and have to a large extent replaced the time-honored reverberatory. The rotating hearth, as in Brueckner's furnace, providing for constant stirring of the material treated and the exposure of new surfaces to the hot gases and air from the fireplace, has in some hands given valuable results in application to this preliminary roasting.

For the amalgamation itself the classical Freiberg process, carried out in revolving wooden barrels, is no longer in use at Freiberg itself, having been given up a few years ago; it is still employed elsewhere, however, as in Chili, and up to a short time ago, at least, at a few works in the United States. The ancient Mexican or *patio* process, the invention of Fray Bartolomé de Medina in 1557, still holds sway throughout most of Spanish America. Its place has been taken in this country by the introduction within a few years of the so-called "Washoe" process of amalgamation in cast-iron pans. These shallow cylindrical or slightly conical pans may be considered as improved

forms of the old-fashioned Chilian mill or "arastra," replacing the clumsy blocks of stone dragged round in a stone trough by mules or oxen, by a machine entirely of iron, having well-proportioned scrubbers or mullers shod with easily removable plates of chilled iron revolving upon similar plates set in the bottom of the pan, and provided with the means of adjusting the distance between the grinding surfaces. Sometimes the bottom of the pan is steam-jacketed in order to permit heating the charge during amalgamation.

Sometimes the only materials introduced are ore, water and mercury; in which case native silver is simply taken up into solution by the mercury, while the chloride, bromide and even sulphide of silver are more or less effectually decomposed by the iron of the pan and by the mercury itself, the reduced metal being then also dissolved to a fluid amalgam. At other works "chemicals" are added to the contents of the pan, these consisting mainly of cupric sulphate and common salt, essentially the same materials as have long been used, the former in the impure shape of "magistral," in the "patio" amalgamation. The ore is placed in the pan in the state of subdivision in which it comes from the stamps, but is more finely ground during the amalgamation, especially during the first part of the process. Transferred to a generally similar pan known as the separator, but with the addition of much more water, the pulp is stirred round and round until the amalgam separates at the bottom and the soluble matter and great mass of silicious and earthy material from the gangue can be washed away, the amalgam being then drained of fluid mercury (holding a little silver in solution), and heated in an iron retort to drive off the rest of the volatile metal. In this process, greatly improved as it is in contrast with patio amalgamation on the score of time and labor consumed,* and in spite of the advantage gained by experience as to details in its application, there is still much room for further economy, the loss being large in absolute value of the precious metal, either not chemically separated from some of its compounds in the ore (imperfect reduction), or not mechanically separated as amalgam from the "tailings" which are washed away (imperfect collection). The value of the mercury also lost is in the aggregate important, some of it losing its metallic form, as it serves as the means of reducing the silver by taking up chlorine, sulphur, &c., some of it being as finely divided metal mechanically washed away.

2. *Smelting processes, involving the reduction of the silver by furnace means, and its collection in solid alloy with one of the baser metals, usually lead, sometimes in the first instance copper.*

The use of improved forms of furnace for both roasting and

*As has been often pointed out, the patio process is applicable in regions where want of fuel forms an obstacle to the use of quicker methods.

smelting lead ores has been already alluded to, and their merits have been tested on a large scale in the treatment of the argentiferous sulphide and carbonate found in such abundance in some of the States in the far West. The further treatment of the "base bullion" or argentiferous lead produced, with a view to the separation of the silver, requires now to be noticed.

The original invention of Pattinson of Newcastle, patented in 1829, for desilverization of lead, depends upon fusion of the metal in somewhat large mass, slow cooling, and removal with perforated ladles of the lead crystals as they solidify, repeating the process several times with the re-fused crystals on the one hand, which become poorer and poorer in silver, and with the residual lead on the other, this increasing in value up to a certain point, when it is cupelled. This mode of working has of late been modified by Rozan, a jet of high-pressure steam being passed into the bath of melted metal, stirring it up and exposing fresh surfaces to the air, so as to promote the oxidation and removal as dross of antimony, copper, &c., while the steam, as it condenses, leads to more regular crystallization than attended the older method. Hydraulic cranes are used in transferring the lead, doing away with much of the arduous hand labor formerly required. The results are favorably reported.

To a large extent, however, for some years past the process known as that of Parkes has been substituted for the ingenious invention of Pattinson. Zinc is added (1–5 per cent.) to the melted lead to be desilverized, the temperature being raised above the fusing point of zinc, and the two metals are well mixed by agitation. A prolonged period of repose follows, extending to several hours, during which the temperature is allowed gradually to fall, so that the zinc separates out on the surface in solid form, carrying the silver with it. The zinc is removed and afterwards distilled off in flask-shaped retorts of plumbago ware, the residual silver being finally fused with a small quantity of lead and cupelled. This Parkes process has become well established in the United States, and has received here some useful improvements in the details of its application.

3. *Processes carried out in the liquid way, the silver, as one of its compounds, being brought into solution and afterwards precipitated.*

These methods have of late years received a moderate degree of extension, although their importance as regards aggregate result is trifling in comparison with amalgamation and smelting. The Ziervogel process, involving the production of silver sulphate by careful roasting of the ore without common salt, and extraction of this sulphate with hot water, has perhaps made more progress than chlorination by roasting

with salt, followed by washing out of silver chloride with brine or solution of sodium thio-sulphate. Experiments have been made in the United States with Plattner's chlorination by means of chlorine gas, followed by leaching to extract silver chloride, and also with Ziervogel's process combined with subsequent amalgamation of the washed residue.

Gold.—The great discoveries of gold in California and Australia, first in the form of sand and nuggets in river gravel, have proved important, not only in the wealth they have afforded within thirty years, and the movements of population and rapid extension of civilization they have given rise to, but in the stimulus given to study of the modes of occurrence of the precious metal and the best methods for its extraction. Not only have existing river-beds been explored, but vast masses of alluvium from water currents that have for ages ceased to flow are washed over, and by mechanical arrangements which, starting from the simple pan in the hands of the laborer in 1849, have culminated in the "hydraulic mining" of the present day, employing sometimes the force of a jet of water six inches in diameter, projected with the pressure due to a head of more than four hundred feet. Before long the attention of the seekers after gold washings was attracted to the veins of auriferous quartz, and gold diggers became gold miners; improvements were made in the mechanical appliances for crushing quartz upon a great scale, and in the amalgamation process for extracting the gold from it; this source of material having for years past grown in importance as the richer stream and dry alluvial works remaining have waned in number and extent. Finally the gold existing in microscopic or even ultra-microscopic particles distributed through masses of pyrites, galena, blende, carbonate of lead, &c., and associated with other ores, as of silver, has come into requisition, and ore by hundreds of thousands of tons is worked which does not contain on an average as much as .0001 of its weight of gold. Much of the ore from even the great "bonanza" of the Comstock lode might not many years ago have passed under the eye of an experienced miner without its containing useful metal of any sort being suspected. The only strongly-marked contrast to such material has been presented by the marvellously rich pockets and small veins of tellurides in Colorado, very limited in extent, but furnishing sometimes small lots of ore worth $40,000 or $50,000 a ton.

The defects, mechanical and chemical, of the processes in use for the extraction of gold lead to immense losses in absolute value, such as may be counted by millions of dollars annually. It has been estimated, by comparison of the results actually obtained on the large scale with those of careful assays, that quartz amalgamation involves a loss of 12 to 15 per cent. of the gold actually present, while probably still

poorer returns are obtained by "hydraulic" treatment of alluvial gravel, 15 to 30 per cent. of the gold *exposed* being supposed to be lost.

The methods for collecting by smelting the generally very small quantities of gold from pyritous ores and those of lead and zinc are essentially the same as in the case of silver, above alluded to, and the same progress has been made of late years; in fact both the precious metals are commonly obtained together in the matte or base bullion, from which the inferior metals are separated by the same operations. Although these smelting processes yield in the aggregate far less gold than is obtained by washing and amalgamation, there is reason to believe that it is obtained with a less proportion of loss.

The chlorination process of Plattner has been used to but a moderate extent. It demands very careful roasting of sulphurous ores as a preliminary step. The use of bromine, now obtainable at a very low price, seems worth attentive consideration, especially if combined, as it might be, with arrangements for recovering the bromine.

As regards the separation of gold and silver from each other, the long known method of "parting" by solution of the latter metal in acid is varied mainly as respects the kind of acid used, European practice having for the most part long since settled down upon hot, concentrated sulphuric acid, while at very large refining works in San Francisco local conditions some time ago caused nitric acid to be preferred, one of these conditions being understood to be the trouble there of disposing of sulphur dioxide economically without nuisance, while the lower oxides of nitrogen can be carried into the furnaces and their oxygen taken up by the fuel.* The immense supply of "argent doré," as the bullion is called which the ores of the Comstock lode in Western Nevada yield by amalgamation, has for several years placed the San Francisco works on a most favorable footing for the application of the parting process, since the bullion contains on an average about 4.75 per cent. of gold by weight in proportion to silver, and therefore needs no addition of the latter metal to secure complete separation by the acid. When gold is the predominant metal, and it becomes necessary to dilute it by further alloy—the old process of "quartation"—in order to avoid cloaking and protection of the portion of the mass which the acid should dissolve, it has not long since been proposed to replace silver, which has hitherto been generally used as the diluting metal, by one of less value, and it has been shown that zinc, added to the extent of five to eight times the weight of the bullion

* In San Francisco, in connection with the employment of sulphuric acid, precipitation of the silver sulphate by a hot, concentrated solution of ferrous sulphate, has been brought into use instead of the metallic copper precipitation.

to be treated, may be very easily alloyed with it at a comparatively low temperature, while nitric acid will afterwards readily dissolve out zinc, silver, copper, &c., leaving the gold fine. If this be brought into use on the large scale, the more costly nitric acid might in all probability be dispensed with by dissolving out the zinc first with diluted sulphuric acid, and then boiling the residual metallic sponge with the same acid in the concentrated state so as to take up the silver and copper.

Much merit attaches to the ingenious chlorine gas process, invented by Mr. F. B. Miller of the Sydney Mint, New South Wales, for separating the two precious metals when alloyed with gold in excess.* He passes a stream of gaseous chlorine down into a crucible containing the alloy in a state of fusion until the silver is converted into chloride, decants this off, recovers a little gold from it by refusion with a small amount of sodium carbonate, and then, casting it into slabs, reduces to metallic silver by means of zinc and a little dilute sulphuric acid. This process, which has since its publication been applied in European refining works, is as well fitted for the special service of dealing on the spot with the large masses of Australian gold bullion, as the San Francisco "parting" is applicable to the silver bullion of Nevada.

Platinum.—The most important change in the method of working the refractory alloy which constitutes what is called native platinum has been the introduction of Deville's process for dealing with it by purely furnace means, avoiding the tedious and expensive solution in aqua regia, and separation by subsequent precipitation as originally proposed by Wollaston, and exclusively practiced since the beginning of the century. The main features of Deville's process consist of fusion with galena and litharge, separation of the osm-iridium left undissolved, cupellation of the platiniferous lead alloy obtained, and fusion of the residue left upon the cupellation hearth by means of a stream of ignited oxygen and hydrogen or coal gas in a furnace of compact lime. Although this method has been used upon the large scale, and much platinum has been worked by it, it is said to have lost favor with the principal manufacturers and to have already fallen out of use. The product obtained by it is not pure platinum,† but an alloy with iridium and rhodium mainly, better capable, it is true, than the pure metal of withstanding the action of acids and other chemical reagents, but harder, less freely malleable, and more troublesome to work mechanically. On the other hand, Deville un-

* This process is also available as the means of toughening such gold as is occasionally found to be brittle and mechanically intractable from the presence of traces of certain of the baser metals, such as lead, antimony, bismuth, &c.

† Nearly, if not quite, all the platinum of commerce contains at least traces of iridium, but in the product of Deville's method of treatment iridium and rhodium occur in quantity varying from 2 or 3 to 25 per cent.

doubtedly deserves the credit of having given practical shape to the *fusion* of platinum in large masses, substituting this more perfect mode of producing compact ingots for the troublesome and less satisfactory *welding* which alone Wollaston had been able to employ. This feature of the new process has become thoroughly established, and will without doubt be permanently retained in use.

Metallic Alloys.

Amongst the most interesting and valuable materials of this class which may be called new, or comparatively new, may fairly be named the following:

Aluminum bronze—a result of the experiments made by Deville upon an industrial scale with metallic aluminum, consists usually of about 90 per cent. copper (which should be of the greatest attainable purity) and 10 per cent. aluminum, although these proportions are subject to variation. It may therefore be looked upon as gun-metal in which tin has been replaced by aluminum. It is distinguished by a bright yellow color which may be made closely to imitate that of gold, by capability of resisting in a very high degree both tensile and compressive strains and abrasive friction, by rigidity and remarkable elasticity, while it readily furnishes sound castings and may be forged with satisfactory results.

Phosphor-bronze—a modified gun-metal, was first produced, and carefully tested on a large scale (after several earlier experiments looking in the same direction by others, as Abel in England and Ruolz in France), by Montefiore-Levy and Kuenzel of Belgium, in 1870–71. It consists of copper and tin, either in the proportions for ordinary gun-metal, viz. 90 per cent. copper and 10 per cent. tin, or, preferably, with an increase in the amount of the former and diminution of the latter metal, some of the best results being obtained with about 5 or 6 per cent. of tin, while in either case a little phosphorus is added. Of this last element, added in the form of a previously prepared phosphide of tin, a variable portion burns out during the fusion of the alloy, but a small amount is retained ranging from a small fraction of 1 per cent. up to a maximum of about 2 per cent. Its effect seems to be threefold, first to eliminate, by combining with, any oxygen which may exist in the copper-tin alloy,* whether as oxide of one or both metals, or occluded in the free state, thus tending to increase and assure the homogeneity and compactness of the alloy; secondly, by supplying a more easily oxidizable element to prevent burning out of tin during the fusion and casting of the alloy, thus rendering the proportion between the two metals more definite

* Phosphorus has also been very successfully used, as phosphide of copper, to aid in the removal of oxygen by the "poling" process for the production of refined and *tough* copper.

and permanent; and thirdly, so far as any phosphorus remains in combination in the alloy, to notably increase its hardness, the effect of even a very small proportion being comparable in this respect with the effect of combined carbon on iron in ordinary steel. The most prominent general properties of the alloy are great tensile strength (in some specimens an increase on that of ordinary bronze in the ratio of 5 to 2), rigidity, hardness, consequent resistance to abrasion, and elasticity. Results of a remarkable character were obtained in trials made, under the auspices of the Belgian Government, of this alloy as the material for field-artillery, although these results were not without drawbacks in regard to this special application. For portions of the machinery of powder mills, and for hand-tools used in such works and in powder magazines, for the cartridge-cases of breech-loading firearms, for pump-cylinders and the screw propellers of sea-going vessels, and with certain changes in the character of the alloy* leading to the pretty uniform distribution of hard metal through a softer basis, for the bearings of shafts and other moving portions of machinery, this material has approved itself as of real value. Its general interest is very great, as opening up a field for investigation in regard to the steel-like modification of alloys of the softer metals.

Manganese argentan or German silver.—The very large consumption of the alloy of copper, nickel and zinc known as German silver, in reality a hardened and whitened brass, as the material for spoons, forks and other articles requiring mechanical strength and rigidity, to be afterwards plated over with silver, has of late years met with interference from the increasing rival demand for nickel to be itself galvanically deposited upon other metals, and a certain degree of importance attaches to the manufacture, at first experimentally by several persons, as Parkes of England and Montefiore-Levy and Kuenzel of Belgium, and since on an industrial scale, of a similar alloy in which nickel is replaced by manganese either wholly or in part, the following being some of the proportions used:

Copper	54.50	55.50	52.25	50.00
Manganese	25.50	13.00	22.25	5.00
Nickel	...	...	...	10.00
Zinc	20.00	31.50	25.50	35.00
	100.	100.	100.	100.

*Addition of lead, which causes segregation of the alloy on cooling into two portions, the one being a hard and tough phosphor-bronze containing very little lead; the other a much softer alloy, consisting chiefly of lead with a small proportion of tin and traces of copper. Railway axle-bearings on the Great Central Railway of Belgium wore out a kilogram of ordinary gun-metal for 99,900 kilometers run, while the same quantity of the phosphor-bronze and lead alloy was worn out for 429,300 kilometers.

Analogous alloys, to which tungsten is also added, have of late been made by Biermann of Hannover. The general character of such material enables it to be used instead of the ordinary German silver, although the hardening tendency of manganese is strongly marked, and unless properly regulated easily leads to trouble from cracking of the alloy in working. The increased tendency to oxidation seems also to call for attention.

Iridio-platinum.—The material finally agreed upon by the International Bureau of Standard Weights and Measures as that to be used in making the new and, it is hoped, permanent standards of weight and length, consists of 90 per cent. platinum and 10 per cent. iridium. It has been produced in masses of magnificent dimensions, one fusion, under the direction of Deville, having turned out 250 kilograms at a single operation, while Matthey, of the firm of Johnson and Matthey of London, has made rules for geodetic measurements, each of 4 meters in length by 21 millimeters wide and 5 mm. thick. The high density of the alloy—21.512 at zero—its malleability, coupled with a considerable degree of hardness, its rigidity and elasticity, capability of receiving a beautifully polished surface and sharp, delicate graduation lines, and its inalterability by any ordinary chemical exposure, all appear to fit it remarkably well for the use being made of it and to justify the choice of the International Bureau; yet it seems fairly to admit of question whether any alloy or any compound or mixture is to be preferred for such a purpose to an elementary metal, such as platinum, about whose homogeneity, uniformity of physical properties, and above all permanence of character, less doubt may well be entertained.

Our knowledge in regard to alloys in general has received valuable extension from the researches of Matthiessen,* conducted more particularly with gold, silver, copper, tin and lead. It is greatly to be desired that his investigations, cut short by too early death, should be resumed, and carried forward with similar intelligence, accuracy, and desire for the discovery of general principles rather than of immediately applicable facts merely.

A recent (1876) observation of a general kind, and novel in itself, has been made by Prof. Silliman in regard to the possibility of conferring sonorous elasticity upon soft alloys, as of tin with antimony, copper, &c., such as "Britannia metal," by a peculiar method of tempering, articles cast from such alloys being immersed for a short time, from a few seconds to a minute or more, in a bath of paraffin oil or melted paraffin, heated to a temperature about 3° C. below the fusing point of the alloy, hence usually to 220°–230° C.

* Brit. Assoc. Rep., 1863; Proc. Roy. Soc. xi. and xii.; Phil. Mag. xiii., &c. Some researches of general interest have lately been published by Roberts on alloys of silver and copper (Proc. Roy. Soc. xxiii), and by Riche on alloys of copper and tin (Ann. Chim. Phys. [iv.] xxx).

Electro-Metallurgy, and other Alterations of Metallic Surfaces.

The practical substitution, on an industrial scale, of dynamo-electric machines for galvanic batteries, in the production of the current needed for electroplating, as may now be witnessed in New York, and doubtless in other cities, is worth noting as one illustration of the more economical series of transformations of the potential energy of coal by which electricity is now made available for useful purposes. The simplicity of application, easily worked arrangements for varying the strength of the current and its adjustment to resistance, and several collateral advantages, as of cleanliness and durability, render these machines very satisfactory. It would be interesting to have a full report on the different forms in use for this particular purpose, with specifications of the first cost, expenditure of driving power, work done, &c.

To the three metals, the deposition of which has for forty years been the chief work accomplished by electro-metallurgy, — viz., copper, silver and gold — has now (since 1870) been fairly added a fourth in nickel, whose successful introduction we owe to Mr. Isaac Adams of Boston. His observation that double salts of nickel and *ammonium* afford solutions from which the metal may be readily thrown down as a coherent and lustrous film, forms the basis of the already important nickel-plating. The nearly white color of the metal, its hardness, superior to that of silver, its but slight tendency to tarnish or rust on exposure to oxygen, sulphur compounds, water, or other commonly occurring atmospheric substances, with its cheapness in comparison with silver or gold, combine to make it extremely valuable for a multitude of applications requiring the protection and concealment of iron, brass, copper and other of the baser metals. In tenacity, hardness, and resistance to chemical alteration, cobalt, which is deposited under like conditions, seems to stand upon nearly the same footing with nickel, while in color it is perhaps superior, being bluish rather than yellowish grey, and when polished presenting a nearer resemblance to silver. The sparing occurrence, however, of cobalt ores, and the large demand for cobalt oxide and silicate in connection with glass staining, porcelain painting, and the manufacture of pigments, tend to limit the scale upon which this metal can be used for plating.

Although the reproduction of engravings was among the first applications of electro-metallurgy, the rapid growth of this application, its expansion in new directions, and the immense extent to which for some years past it has been made serviceable in connection with printing, both of matter at first set up with movable type and of engraved work of the most various kinds, cannot be overlooked amongst novel features of modern industry. In this direction both forms of electro-

metallurgy are made useful; the superficial coating of one material with another, as in the harder surface given to ordinary type by the deposition of copper, nickel, and even occasionally iron; and the plastic reproduction of an engraving or a page of type, multiplying with wonderful rapidity and perfect accuracy the printing surfaces from which the myriad impressions upon paper are to be stricken off.

There still remain some applications of the electric deposition of metals obviously desirable but not yet satisfactorily made. One of these as yet unsolved problems seems to be the production of a really good calico-printing cylinder, of cheaper material than massive copper, and having the intaglio pattern accurately and rapidly transferred to the surface by electro-metallurgy. Improvements in the means of treating the existing cylinders, removing old patterns from them and replacing by new ones, have diminished the importance of this question, but it still remains worthy of examination.

With regard to other alterations of the surface of metals, partly mechanical and partly chemical, the last few years have seen continued and rapid extension of long known processes, such as the tinning of sheet iron, which has received the stimulus of enormous demand for the product arising from the employment of "canned" provisions on a scale far beyond that of even ten or fifteen years ago; the coating with zinc or so-called "galvanizing" of iron, which has been in considerable degree stimulated by the stretching forth of scores of thousands of miles of telegraph wire and the increasing use of iron roofing; the production of "malleable" iron castings for innumerable purposes, especially house fittings and builders' furniture, locks, hinges, and the like, the softening of which by superficial burning out of carbon is effected with noticeably greater success and uniformity than used to be attained; and the opposite manufacture of articles of forged iron "case-hardened" by superficial addition of carbon to form a steely coating, mechanics' tools of various sorts furnishing a wide field for the cheap and useful application of this alteration of surface.

Among the more novel industries of this sort may be mentioned the recently (1877) introduced process of Barff for protecting iron from rust by exposure to superheated steam at predetermined temperature and for a properly regulated time. The result is the coating over the surface with a very hard and closely adherent layer of magnetic oxide. That this general result is not in itself new is manifest, a thinner coating of the same sort having long been used for the same purpose, upon parts of fire-arms for instance, and the comparative exemption from rust of the black surface of iron bars from a rolling mill and fresh forged work from the blacksmith's hammer being due to the same cause. In this respect the

florid language used by sundry reporters of the supposed new invention is far from being justified. But real merit undoubtedly attaches to the special method by which the object in question is secured,* and to the care with which the details seem to have been worked out. It is stated that if superheated steam at 500° F. be used, and the exposure of the articles to be protected be continued for five hours, a surface is obtained which will resist emery paper for a considerable time, and which will not rust within doors after any moderate degree of exposure to moisture; while, if the oxidizing process be conducted at 1200° F., and continued for six or seven hours, the surface will resist a rasp, and will bear prolonged exposure to the weather out of doors. The oxidation does not affect the appearance of the surface otherwise than by turning it black, the texture of the surface remaining unaltered, whether it be that of a rough forging, of a turned or a polished object.

There can be no doubt that for many purposes the protection against rust thus given the surface of iron will be valuable, and if the assertions made in regard to the thoroughly firm adhesion of the film of magnetic oxide, even under conditions of greatly and rapidly varied temperature, prove to be sustained, and the anticipations of the inventor of the process, that it may be applied to the plates of steam boilers, and of iron ships, be successfully carried out into practice, this may perhaps be ranked as one more of the not very numerous list of methods, of first-class importance, for usefully modifying the surface of worked metals.

J. W. MALLET.

[*To be continued.*]

ANIMAL CHEMISTRY; OR, THE RELATIONS OF CHEMISTRY TO PHYSIOLOGY AND PATHOLOGY. By Charles Thomas Kingzett, F. C. S. London, 1878. Pp. 494.

The object with which this book was written is not at first quite obvious, since, in spite of its dedication to medical men and scientific chemists, it is clearly not suited for either; it is too full of uninteresting and, so far as we know at present, unimportant minutiæ for the physician, and too meagre in technical details for the chemist, who will not find it in any degree adequate to replace the well-known manuals of Hoppe-Seyler or Gorup-Besanez. A little examination, however, serves to show without much doubt that the real object of Mr.

* Mr. G. Bower has also experimented upon the production of a coating of magnetic oxide by exposure of the iron to heated air at regulated temperature, and by like exposure to air mixed with carbon dioxide (gaseous products of combustion), followed by a stream of carbon monoxide, which leads to ferric oxide being first formed, to be afterwards reduced to the magnetic oxide.

Kingzett's publication is the glorification of Thudichum; Allah-il-Allah — there is but one physiological chemist and Kingzett is his prophet. Gratitude in a pupil is an admirable trait, but it should be kept within bounds; which is hardly the case when it leads to the production of a manual in which the foremost living workers are ignored or sneered at, while the beloved teacher is not only constantly quoted for what he has done, but given as the authority for what he has not. The effect is, in truth, somewhat ludicrous when Thudichum is dragged forward as the sponsor for all sorts of opinions which have long been the commonplaces of the physician or physiologist. As examples, take the following:—"According to Thudichum, the spleen contains much blood"—"Thudichum points out that in leuco-cythæmia the spleen is frequently large"—"Thudichum states it is probable that improper nutrition has the main share in causing these diseases (scrofula and tuberculosis) in many children."

A far more serious defect, however, is the author's entire ignorance of physiology, which crops to the surface in almost every page, and in reference to almost every subject. When he tells us that from Frerich's researches it would appear that Peyer's glands contribute but slightly to the formation of intestinal juice, it is pretty clear that he has no idea what a so-called Peyer's gland is. When he writes that "there can be no doubt that the principal function performed by the liver consists in the elaboration of bile and its secretion," he will find but few physiologists to agree with him. The statement that the colorless corpuscles of the blood are "constantly vibrating" proves pretty conclusively that he never saw the bodies he is writing about, while the researches of the last few years are altogether ignored in the statement that sweat is nothing more or less than a liquid exuded from the blood-vessels. We were rather of opinion that it has been satisfactorily proved that sweat, although its materials are derived from the blood, is in no way an exudation, but a true secretion formed by the gland-cells under the influence of certain nerve fibres. However, ignorance of comparatively recent work is more or less excusable; but when we come to the subject of respiration and find Mr. Kingzett still living mentally in the age of Lavoisier, we find an ignorance which is quite unpardonable, although one is perhaps inclined to be less severe on account of a feeling that the author is, after all, an object of pleasant antiquarian interest. If there is one question in animal chemistry which seems beyond dispute, it is that oxidation takes place no more in the lungs than elsewhere, in fact rather less; and nearly all are now agreed that the main oxidative processes in the body take place in the living tissues and not in the circulatory blood. But read the following extracts:—

"Alcohol . . . a respiratory food, or a substance which ad-

mits of oxidation in the lungs," p. 153. "Modern researches tend to show that vitality consists more in changes occurring in the blood," p. 198. "The source of vital force, viz. blood oxidation," p. 181. It is true the contrary doctrine is referred to as held by various authorities, but several pages are given up to expounding with approval the views of a Dr. Hake, who seems to be an extreme supporter of the Lavoisian doctrine, and who holds that "the oxidation of carbon and hydrogen in the lesser circulation is (was) the source of muscular in common with all other vital force"; and again, that "the cerebro-spinal system does not generate its own force, but derives it through the chemical changes in the lungs." Further, Dr. Hake believes (p. 181) that the brain is a great storehouse of energy, whence it is transmitted to the muscles, glands and so on, and Mr. Kingzett seems to think this quite plausible. It is enough to make Haller turn in his grave to have his labors ignored in this way, and to find in the nineteenth century the nervous system spoken of as supplying the muscles with their contractility.

It would be a long task to point out the misstatements which meet us in every chapter. It is, however, only fair to Stokes to point out that he did not demonstrate that arterial blood gave a spectrum with two absorption bands while venous blood exhibits but one. Every physiologist knows that ordinary venous blood gives the two bands, and that the single band only appears in the blood of asphyxia.

We cannot conclude without quoting the description of the structure of the teeth, which will delight histologists:—"Indeed, the roots or stumps of the teeth are bones, properly so-called. The exposed parts of the teeth, however, consist of many minute tubes of peculiar construction, and composed of what is called dentine; over this there is a harder epithelium structure called cement."

In a preface the author states that the book was written to complete a connection with studies in physiological chemistry which had been attended for four years with unfluctuating success. We regret we cannot congratulate him on the success of his crowning effort. Should he again contemplate resuming such studies, we beg him first to learn a little physiology: he would probably be surprised to find how useful it would be to him.

H. Newell Martin.

The Chemical Composition and Physical Properties of Steel Rails. By Charles B. Dudley, Ph. D., Chemist of the Pennsylvania Railroad Company, Altoona, Pa.

This memoir was originally prepared as a report to the Pennsylvania Railroad Company, and has been since presented

to the American Institute of Mining Engineers and published in its Transactions. The paper is mainly devoted to an account of the chemical composition (as to C, Si, P, and Mn) and certain of the physical properties of twenty-five samples of steel rails, whose history has been recorded in reference to the positions they occupied on the road-bed, amount of tonnage which passed over them, extent of wear, giving way or not by fracture, &c. The work of examining these steel specimens seems to have been carried out with care, and the results, both as given in detail and as tabulated in condensed form, may be studied with much interest.

As regards the physical conditions involved, it is to be regretted that the tests made of tensile strength, elongation before rupture, angle of torsion, &c., seem to have been applied only to the worn and in some instances fractured rails which had been removed from the road and were submitted to analysis. It would have added much to the interest and practical value of these tests had they been also applied beforehand to the rails when new and as yet unused. It can hardly be supposed that the original character of a piece of steel was represented by its behavior under physical tests applied after it had been in service for ten years, and had endured the passage over it of 37,005,142 tons.

The chief point in the discussion of the chemical result which seems fairly open to criticism is the mode adopted of expressing the sum of the elements found (other than iron) in terms of what the author calls "phosphorus units"; .01 per cent. of phosphorus being taken as such a unit, and the assumption made that an equal effect in hardening steel and rendering it brittle is produced by .02 per cent. of silicon, .03 per cent. of carbon, and .05 per cent. of manganese, so that "the phosphorus units are found by adding together the phosphorus, one-half the silicon, one-third the carbon, and one-fifth the manganese, expressed in hundredths per cent." The author admits that he does not know of any definite relations having ever been discovered between these substances in this respect, and furnishes no reasons for his arbitrary assumption of the above figures, thus reducing the value of the conclusions he draws as to the united effect and distribution of effect of these ingredients. In view particularly of the great importance attaching to the influence of carbon and phosphorus respectively upon steel,* and to the capability of in a sense mutual replacement which these ingredients seem to possess, it is desirable to obtain results as

*The problem of sufficiently removing phosphorus from cast iron containing it in large quantity, so as to make good steel, alluded to in the April No. of this Journal, foot-note to p. 65, seems to have a chance of satisfactory solution in the experiments now being carried out upon a large scale by Messrs. Bolckow, Vaughan & Co. in England upon the application of the Bessemer process with lime-lined converting vessels to pig-iron made from Cleveland ore.

far as possible uncomplicated by assumptions like those just mentioned.

The value, however, of such experiments as the author has made lies mainly in the data which they afford for future comparison with such others as may hereafter be accumulated; and in the publication of the results of accurate quantitative measurements, chemical and physical, instead of more or less vague estimates merely of the character and behavior in service of steel for railroad use, Dr. Dudley has done good work. One of his conclusions calls for special attention and comparison with similar observations elsewhere, namely that some at least of the harder rails wore away more rapidly in service than those of softer steel. This is in accordance with certain results lately reached in England. In regard to this very important point, capability of withstanding abrasion, it seems by no means likely to be a matter of indifference whether the hardening of the metal be effected by carbon alone or mainly, chiefly by phosphorus, silicon, &c., or by several such elements present together in varying proportions. J. W. M.

FOREIGN PHOSPHATES. By Dr. Charles U. Shepard, Jr. Charleston, S. C. 1879.

This pamphlet, the report of a public lecture delivered to a popular audience, contains a useful survey of the world's chief sources of supply at present of the various materials — bones, recent and fossil; so-called coprolites; guanos and rock-guanos; mineral phosphorite, apatite, &c.—capable of yielding phosphoric acid for agricultural use. Its interest is increased by some details as to the principal European localities affording phosphates, the results of personal observation by the author on a recent visit to these deposits. The large veins of Spanish phosphorite, especially at Logrosan in Estremadura, the excellent quality of the material they afford, and the low price at which it may be furnished when legal injunctions now preventing work shall be removed, are spoken of in very high terms. J. W. M.

ELEMENTARY QUANTITATIVE ANALYSIS. By Alexander Classen, Professor in the Royal Polytechnic School of Aix-la-Chapelle. Translated by E. F. Smith, A. M., Ph. D., Assistant in Analytical Chemistry, University of Pennsylvania. Published by Henry C. Lea.

This work is constructed on the same plan as Woehler's *Mineral-Analyse in Beispielen*. It consists almost wholly of clear and specific directions for the analysis of particular compounds, alloys and mixtures, which have been selected as

examples to illustrate the best methods of quantitative determination and separation. These examples have been chosen with such excellent judgment that they involve a wide range and large variety of quantitative work, without being too numerous for the ordinary student, for whose guidance the work is intended. It is obvious from the plan followed that the author believes, with Woehler, that "it is easier for most heads to reach a clear comprehension of general relations and rules through the consideration of a specific case, than to accommodate themselves to the application of general rules and principles to special cases." To those who concur in this opinion the book will recommend itself as one of more than ordinary merit. H. N. MORSE.

NOTES.

Note to Paper on Nitrogen Iodide in April Number of this Journal.

It is interesting to compare the formula suggested for nitrogen iodide and the various substitution products from it containing hydrogen with that given by Zorn (*Ber. d. chem. Gesell.* 11, 1630) for the compound he obtains by the action of ethyl iodide upon nitrosyl silver, which he views as diazoethoxane, and describes as "almost as explosive as nitrogen chloride." Griess (*Ber. d. chem. Gesell.* 10, 528) has proposed to consider other diazo-compounds as containing pentad nitrogen. J. W. MALLET.

Malleable Nickel and Cobalt.

TH. FLEITMANN has succeeded in obtaining the metals nickel and cobalt in malleable condition by fusing them with a very small quantity of metallic magnesium. He suspected that the absorption of carbon monoxide by the metals might be the cause of their want of malleability, and introduced the magnesium for the purpose of destroying the gas, as this metal is known to decompose the oxides of carbon. The success was very surprising. An addition of $\frac{1}{2}$ per cent. of metallic magnesium changes the structure of the metals entirely. They

can now be easily welded when hot. Nickel is malleable even when cold, while cobalt becomes extremely hard when cold, so that it will probably be applicable for cutting instruments.

At the same time the cast metals are very compact, and are almost as solid and tough as cast steel, so that the metallic parts of harness and similar objects may be made from them.

Both metals take a very high polish, and resist the action of the atmosphere very well. The author has also succeeded in welding malleable nickel and cobalt together with steel and iron, so that the pieces of iron and steel that are coated on one or both sides with nickel or cobalt may be beaten out to the thinnest plates without any separation of the metals.

Magnesium also causes a remarkable change of structure in other metals. A coarse-grained steel becomes fine-grained on the addition of one-fifth per cent. of magnesium. In performing the experiments referred to, the magnesium must be introduced through a hole in the cover of the crucible after the oxygen has been first removed by the addition of a few pieces of charcoal. Without this precaution violent explosions are apt to occur.—(*Ber. d. chem. Gesell.* 12, 454.)

Stop-Cock of easy Construction.

In the *Zeitschrift f. analytische Chemie*, 18, 258, is described a simple form of stop-cock, made of glass tubes and corks, devised by Lecoq de Boisbaudran. A much simpler form may be constructed as follows:

Take two glass tubes, one of which slides easily into the other, close the end of the smaller tube in the flame of a Bunsen's burner, and make an opening about an inch from the closed end by filing crosswise with a rat-tail file. Connect the two tubes by a piece of rubber tubing, which should fit the smaller tube closely, and the stop-cock is complete. When the smaller tube is pushed into the larger one the cock is open, when shoved back into the rubber tube the opening in the small tube is covered by the rubber wall and the passage of liquids or gases prevented. The accompanying figures make this clear. Fig. 1 represents the cock open. Fig. 2 shows the cock closed.

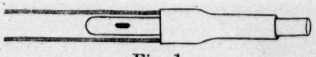


Fig. 1.

Fig. 2.

EDWARD HART.

Treatment of Bunsen's Elements.

In order to keep the metallic connections of galvanic batteries bright, and thus keep the batteries in good running order, BEILSTEIN and JAWEIN recommend the use of *oleonaphtha* as a lubricant. This material is obtained in large quantities from Caucasian petroleum and is sold at a moderate price.* The connections remain unchanged for a long time. Not the least formation of rust was noticed on the binding screws which were on the charcoals placed in nitric acid.—(*Ber. d. chem. Gesell.* 12, 448.)

Analysis of a Calculus found in a Deer.

This rather interesting specimen was given me by Mr. Hall, student in the Medical Department of the University. It was found by him in the pelvis of the kidney of a doe, which had been shot by a party hunting in the northwestern portion of this State.

As the investigation of such calculi very frequently affords some interesting results, I subjected this specimen to both a qualitative and quantitative examination.

The size of the calculus was equal to that of the egg of a pigeon. It possessed a fawn color, and consisted of three layers encircling a rather large nucleus, which presented a granular sandstone-like appearance. The layers were exceedingly thin, and seemed to have grown out from carbonaceous deposits, which were detected in various portions of the calculus.

Upon testing the nucleus qualitatively the presence of silica, ferric oxide, calcium oxide and phosphoric acid was clearly shown. The surrounding layers were found to contain calcium and magnesium oxides, phosphoric acid, sodium, potassium, uric acid and another organic compound. The latter was extracted from the finely divided material by boiling the same for some time with alcohol. The alcoholic filtrate yielded upon evaporation a gelatinous mass, which proved to be the sodium salt of an acid, which formed strong, colorless needles, exhibiting an hexagonal structure. Upon gently warming this crystalline mass with a grain or two of sugar and a drop of concentrated sulphuric acid, a beautiful purple color appeared. It is true, several acids occurring in the bile give the same reaction with sugar and sulphuric acid, but not any of them, so far as I know, possess the crystalline form of the above compound, nor yield a sodium salt similar to that mentioned above. The only acid which in the least corresponds to the previous description is that known as *lithofellic acid*, which was discovered a number of years ago† in a va-

*Probably the lubricating oil obtained from petroleum in this country would answer the purpose equally well.—ED.

†Ann. der Chemie, 39, p. 237, 242; 41, p. 150.

riety of the deer family. The want of sufficient material prevented me from making other and more decisive tests to discover the real character of this compound.

As the layers surrounding the nucleus were alike in chemical composition they were finely divided, and a quantitative analysis made of the mixture. Analysis:

43.15	per cent.	P_2O_5.
.91	"	MgO.
2.60	"	Loss on ignition.
2.50	"	CaO.
51.00	"	alkaline oxides.
100.16		

EDGAR F. SMITH.

Note on the Absorption Spectrum of Uranine.

Having only a small quantity of uranine, I took for the experiment .0038 gram. I dissolved this quantity in 500 cc. of water and examined in a glass cell 12 mm. in diameter. .0038 g. in 500 cc. gave almost black band, the extreme edge of which is almost coincident with the F line of the solar spectrum. The absorption band extended from this point almost half way through the green. .0038 g. in 1000 cc. gave a distinct band. .0038 g. in 2000 cc. gave still a distinct band. .0038 g. in 4000 cc. gave a faint yet readily detected band. .0038 g. in 8000 cc. gave no distinct absorption.

From the above it is seen that one part of uranine in one million parts of water is readily detected by its deportment in the spectrum. By increasing the thickness of the liquid traversed the delicacy of the reaction could be made more striking. I employed indirect sunlight for producing the spectrum, and Vogel's spectroscope in the observations. The examinations were made immediately after the solution of the substance.

H. W. WILEY.

*Note on the Delicacy of the Test for Cobalt with Cyanide of Potassium and yellow Sulphide of Ammonium.**

Mr. G. L. SPENCER has made some experiments to determine the limit of the above-mentioned reaction for cobalt. .0924 g. cobaltous nitrate was dissolved in 100 cc. of water. 1 cc. of the solution in 1 cc. of water on addition of the reagents gave a pronounced red color. .2 cc. in 1 cc. of water gave still a distinct red color. .15 cc gave in 1 cc. water a faint red color. .1 cc. in 1 cc. water did not give an appreciable red tint.

Thus it is seen that less than one-tenth of a milligram of cobaltous nitrate in 1 cc. of water can be easily detected by

* Tattersall, Chem. News, Feb. 14, 1879.

the above method. This quantity evaporated to dryness and collected as fully as possible failed to give a blue color with a borax bead. Sulphide of ammonium and cyanide of potassium are therefore more delicate reagents for cobalt than borax. The presence of zinc, nickel and manganese salts diminishes slightly the delicacy of the reaction. One milligram of the cobalt salt, however, in 1 cc. water was still to be detected in the presence of three hundred times that weight of the compounds of the other three substances. I am having my students use this method and with satisfactory results.

H. W. WILEY.

New Compounds of Ammonia with Hydrochloric Acid.

In studying the vapor densities of ammonium compounds L. TROOST has been led to the discovery of a number of curious compounds of ammonia with hydrochloric and other acids both inorganic and organic. Two new compounds of ammonia and hydrochloric acid are described. To obtain them, ammonia gas, pure and perfectly dry, is saturated with pure hydrochloric acid gas. The ammonium chloride thus formed is distilled in a closed vessel in the presence of a large excess of ammonia gas, and the products cooled at varying temperatures. Two definite crystalline substances were obtained. The first has the formula $HCl, 4NH_3$, and is called by Troost tetra-ammonia chlorhydrate. It is anhydrous and melts at $+ 7°$. Its crystals strongly depolarize light and consequently do not belong to the same system as those of ordinary ammonium chlorhydrate. If the tension of ammonia given off by this substance be measured, it is found to remain constant for a given temperature, while the volume of gas existing at the surface of the dissociating substance is varied; just as the tension of water vapor in presence of liquid water remains constant for a given temperature with varying volume. This characteristic the author considers sufficient of itself to prove the definite existence of the substance described. Its tension of dissociation ranges from 140 mm. at $-36°$ to 1800 mm. at $+8°$.

The second substance obtained has the formula $HCl, 7NH_3$. It melts at $-18°$, but may be cooled to $-40°$ before solidification. The author was unable to distinguish its crystalline or optical properties from those of the preceding substance, but its appearance was quite different. The characteristics of its dissociation were the same as in the case of tetra-ammonia chlorhydrate, into which it is transformed by loss of ammonia. Its tension of dissociation ranges from 580 mm. at $-36°$ to 1130 mm. at $-21°$. The author thinks that this is not the last term of this singular series. He was arrested at this point only by the difficulty of maintaining lower temperatures

constant. Analogous compounds with other acids are to be described in a future communication.—(*Compt. rend.* 88, 579, March 17th, 1879.)

Vapor Density of some Inorganic Bodies.

VICTOR MEYER and CARL MEYER have begun to apply the method recently described by them for the determination of vapor densities, to the study of some difficultly volatile inorganic bodies. Phosphorus pentasulphide, fusing at 274°–276°, and boiling, according to Hittorf, at 530°, was converted into vapor in an atmosphere of nitrogen. The results obtained correspond to the vapor density 7.63 and 7.67, while the formula P_2S_5 requires 7.67. Hence it is seen that the pentasulphide *does not suffer dissociation* when converted into vapor, but that its vapor consists of molecules of the composition P_2S_5.

Since Bunsen determined the specific heat of indium this metal has been classed with aluminium and not with zinc as previously. No compound of indium had ever been converted into the form of vapor, and hence it was not known whether the chloride is analogous to those of iron and aluminium, *i. e.* In_2Cl_6; or has the simpler formula $InCl_3$, or, in other words, whether indium is quadrivalent or trivalent. The authors have now determined the specific gravity of the vapor of indium chloride and obtained the number 7.87. The formula $InCl_3$ requires 7.60, and In_2Cl_6 requires 15.20, so that it is plain that analogy does not exist between this chloride and those of iron and aluminium; and indium is seen to be trivalent. The conversion of the chloride into vapor was effected at red heat.—(*Ber. d. chem. Gesell.* 12, 609.)

Purification of Mercury.

In the last number of this Journal, page 68, a method recommended by Bruehl for the purification of mercury is briefly described. LOTHAR MEYER now describes another method for which he claims certain advantages over the method of Bruehl. It consists in allowing the impure mercury to fall through a solution of ferric chloride. The solution is placed in a glass tube from a meter to a meter and a half long and three cm. wide. The lower end of the tube is placed in a cylinder which has a side opening at the top. As the mercury passes through the solution it breaks up into very fine drops, which do not flow together because they are covered with a very thin coating of chloride or subchloride. The following portions of mercury, however, press them together. The mercury purified by this method is pure enough for use in capillary experiments.—(*Ber. d. chem. Gesell.* 12, 437.)

On the Preparation of Barium from Barium-amalgam.

Some years ago Crookes described a method for the preparation of metallic barium from the amalgam. The amalgam is readily prepared by adding sodium-amalgam to a saturated, aqueous solution of barium chloride. When the amalgam is distilled, mercury passes off, and a substance is left behind which Crookes described as the metal barium. DONATH has repeated the experiments of Crookes, and finds that the product obtained is by no means barium, but rather an amalgam containing a considerable amount of barium. In different specimens there were found 62–77 per cent. of mercury. It is not possible to obtain a purer preparation even in a porcelain tube heated nearly to white heat. Now and then small pellets of a bronze-colored metal were obtained, but this color did not appear in the interior of the pieces. Nevertheless the color of pure barium is yellow, as Bunsen and Matthiessen state in describing the metal prepared by the electrolysis of the fused chloride.—(*Ber. d. chem. Gesell.* 12, 745.)

On the Relations of Cantharidin Derivatives to the Ortho-series.

J. PICCARD has found that when the commercial article, cantharidin, is heated with phosphorus pentasulphide, a very good yield of orthoxylene is obtained. The hydrocarbon yields by oxidation with nitric acid, first, orthotoluic acid, and, by further treatment, phthalic acid. This method is by far the most convenient for the preparation of small quantities of pure orthoxylene. The relation between cantharidin and orthoxylene is similar to that which exists between camphor and cymene (paraethylmethylbenzene), the former being readily transformed into the latter by treatment with phosphorus pentasulphide.—(*Ber. d. chem. Gesell.* 12, 577.)

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